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ROVER FUEL ELEMENT DEVELOPMENT ACTIVITIES

Space Nuclear Systems Office

Purchase Order SNC-95

July-September 1971

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J. M. Napier
G. B. Marrow

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NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

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OAK RIDGE Y-12 PLANT
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Space Nuclear Systems Office

Purchase Order SNC-95

July-September 1971

J. M. Napier

G. B. Marrow

OAK RIDGE Y-12 PLANT

P. O. Box Y, Oak Ridge, Tennessee 37830

**Operated for the U S Atomic Energy Commission
by Union Carbide Corporation—Nuclear Division
under Contract W-7405-eng-26**

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SUMMARY

Experimental studies designed to fabricate NERVA graphite fuel elements capable of cyclic operations at exit gas temperatures of approximately 4,400° R were continued during this report period. Carbon precursor materials, manufacturing parameters, and deposition of metal carbide films are included in these studies. Accomplishments during this quarter include the following:

1. Three commercial powders were extruded into elements having a desirable coefficient of thermal expansion ($\sim 7.7 \times 10^{-6}$ in/in/°C, 25 to 1,000° C).
2. Molded graphites using low-fired filler carbons and uncured short organic fibers produced graphites having an improved strain-to-failure value ($\sim 7,000$ μ in/in).
3. Thick-walled tubes of vapor-deposited zirconium carbide were produced, and the chemical composition was determined. Representative samples were shipped to LASL for determination of the coefficient of thermal expansion.
4. Vapor-deposited zirconium carbide coatings were applied to fuel-element bores.
5. Experimental graphite fuel elements were hot-gas tested; an improved quality was detectable with the application of an increased zirconium carbide deposition temperature.
6. Uranium-loaded ion exchange beads survived a heat treatment cycle of 2,800° C for three hours.
7. Organic precursor carbon studies were oriented toward modification of the CAI polymers.

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INTRODUCTION

One goal of the NERVA program is to produce a reactor capable of operating up to 60 cycles with run durations of ten minutes per cycle. As part of the development of this engine, graphite fuel-element technology has continued to be studied. Alternate fuel element designs are being investigated by other laboratories.

The major problem areas include binders, carbon precursor sources, pressure carbonization, metal carbide coating of bores, characterization of various physical properties of elements and metal carbide tubes, and evaluation of element performance.

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EXTRUSION STUDIES

The primary goal of these studies is to produce a graphite fuel element having high density, low modulus, and a high coefficient of thermal expansion. All of the filler carbons used during this report period were commercial isotropic powders, fired at 900 or 1,000°C. These studies have used binders consisting of ITX-ACN-1 and other graphitizable resins. In all cases, the binder has been a thermoplastic type which produces a graphite structure when heated to nominal fuel-element temperatures.

Nonfueled matrices were extruded that have CTE values equal to or greater than zirconium carbide. A major difficulty encountered was matrix cracks. To reduce the matrix cracking problem, an experimental pressure bake system was installed. Pressure baking of elements at 300 to 350 psi and up to 700°C produced an increased carbon yield from the thermoplastic binder (maximum of 84%) and reduced but did not eliminate the matrix cracking problem.

NONFUELED EXTRUSION STUDIES

Three low-fired isotropic carbon fillers were used in the extrusion studies during this report period. Table A-1 presents a brief description of the extrusions. Table A-2 defines the fillers and the purity of these materials. Two graphitizable resins were also used in these studies. The coefficient of thermal expansion of these elements were equal to or greater than the CTE value of zirconium carbide. The major problem encountered was internal cracks in the element matrices.

FILLER CARBONS

Three low-fired commercial carbon fillers are being used in the present studies. Analysis of the powders (Table A-2) showed that the GLC 1076 powder contained the lowest metallic impurities with iron being the major contaminant (300 ppm). The percent sulfur was about equal in the three powders (~ 1.1%). The GLC 1076 and PCD-0Q were prefired to 1,000°C, whereas the PCD-9 was fired to 900°C. All powders were finely ground with greater than 80 percent of the particles having a size of less than 325 mesh (44 microns).

BINDERS

Three binder systems were used in these studies. One binder consisted of ITX-ACN with a diluent of indene (15 pph); the same binder was used with a diluent of toluene-xylene (15 pph total). A third binder was a commercial material labeled QX 309-1 (Quaker Oats, Chicago). The binder level was varied in an effort to reduce the matrix crack problem.

Table A-1
NONFUELED ELEMENT STUDIES⁽¹⁾

Extrusion Number	Filler	Formulation	Amount (pph)
<u>Ambient Pressure Carbonization</u>			
683	PCD-0Q	ITX-ACN-I	42
684	PCD-0Q	ITX-ACN-I	40
685	GLC 1076	ITX-ACN-I	37
686	PCD-9	ITX-ACN-I	42
687	PCD-9	ITX-ACN-I	40
<u>Pressure Bake Studies</u>			
688	PCD-9	ITX-ACN-I	40
689	PCD-9	ITX-ACN-I	36
690 ⁽²⁾	PCD-9	ITX-ACN-I	38
691 ⁽²⁾	PCD-9	ITX-ACN-T-X ⁽³⁾	39
692 ⁽²⁾	PCD-9	QX 309-1	36
693 ⁽²⁾	PCD-9	ITX-ACN-T-X ⁽³⁾	36
694 ⁽²⁾	PCD-9	QX 309-1	36

(1) One to two elements were made in each test; all were experiments to study matrix cracks.

(2) Powder predried at 250° C for 72 hours.

(3) Toluene and xylene diluent added to binder formulation.

AMBIENT PRESSURE CARBONIZATION

It has been standard practice to extrude the elements and then process the parts using an air cure to 250° C cycle followed by an inert atmosphere heat treatment to 850° C. A large number of elements, processed in this manner, contained visual cracks (longitudinal and transverse). In this process, a coking yield of the binder in the elements is dependent on several factors, but a value of 50 percent is considered typical for the ITX-ACN-I binder. Table A-1 lists the extrusions made using the ambient pressure carbonization cycle. Neither the use of the three powders nor the reduction in binder content solved the element longitudinal and transverse crack problem.

Element sections were taken and heat treated to 2,300° C for one hour to graphitize the matrices. The coefficient of thermal expansion was determined and all three flours produced approximately the same CTE of 7.7×10^{-6} in/in/° C (20 to 1,000° C).

PRESSURE BAKE STUDIES

Thermoplastic, oxygen-free resins, when heated under pressure, will produce a higher carbon yield as opposed to ambient pressure carbonization. An experimental, high-strength, thick-walled, stainless steel tube was fitted

Table A-2
POWDER ANALYSIS

Flour	GLC 1076 ⁽¹⁾	PCD-0Q ⁽²⁾	PCD-9 ⁽³⁾
Surface Area (m ² /gm)	5.2	13.9	7.75
Helium Density (gms/cc)	1.90	1.98	1.92
Particle Size Analysis Screen (%)			
+ 60 Mesh	< 0.1	0.1	0.1
- 60 + 100 Mesh	0.4	0.1	0.2
- 100 + 140 Mesh	1.2	0.3	0.39
- 140 + 200 Mesh	0.8	3.5	5.2
- 200 + 270 Mesh	1.1	9.0	0.2
- 270 + 325 Mesh	1.1	6.3	1.0
- 325 Mesh	95.4	80.6	92.5
Micromerograph			
Percent Less Than Indicated (μ)			
100	-	72	100
90	-	52	63
50	-	7.8	24.5
25	-	4.4	7.8
10	-	2.8	3.65
Loss at 100° C (%)	-	0.38	0.37
Ash (%)	-	0.42	0.65
Sulfur (%)	1.05	1.1	1.18
X-Ray Diffraction (2,800° C fired)			
Interlayer Spacing (Å)	3.363	-	-
L _c (Å)	118	-	-
L _a (Å)	168	-	-

Table A-2 (Continued)

Impurities (ppm)			
Ag	-	-	< 1
Al	25	70	65
B	< 1	2	< 1
Ba	6	-	12
Be	-	4	< 1
Ca	25	60	90
Cd	-	-	< 1
Co	< 20	-	< 20
Cn	25	10	85
Cu	15	-	15
Fe	300	1,000	4,500
K	20	60	20
Li	< 10	< 10	< 10
Mg	< 10	30	100
Mn	3	25	40
Mo	< 1	1	1
Na	40	12	30
Ni	50	35	100
P	< 100	-	< 100
Pb	5	70	6
Si	55	500	225
Sn	-	50	10
Ti	< 6	6	20
V	50	70	125
W	< 10	30	< 10
Zn	< 60	-	< 60
Zr	3	< 2	4

(1) Powder supplied by WNCO.

(2) Typical data of one of the three lots of powder; temperature at 1,000° C.

(3) Temperature at 900° C.

with the necessary flanges and valves to permit coking to 700° C at a pressure of 300 to 350 psi. The tube was inserted into the standard fuel-element carbonization furnace. Early scouting runs are in progress to determine the effectiveness of this operation. The elements carbonized in this manner are also reported in Table A-1.

The early data shows that a pressure coke operation practically eliminated the longitudinal and gross transverse crack problem. The carbon yield of the binder was increased; and, in one experiment, a yield of 83 percent carbon was obtained from a binder of ITX-ACN-I. However, small internal matrix cracks are present in the elements.

Scouting experiments are in progress to define the cause of the small cracks. The indene diluent was changed to a mixture of toluene-xylene. This diluent mixture can be evaporated from the matrix easier than the free-indene diluent. A reduction in the overall binder carbon yield occurred, but carbon yields of greater than 60 percent were obtained. The cracks were reduced in size using this diluent but they were not eliminated.

Elements with both the indene and toluene-xylene diluents were processed through a low temperature operation (maximum 100° C) in an air environment in an effort to eliminate the free diluent prior to pressure carbonization. The number and size of the macrocracks were reduced but they were not eliminated.

A time-to-temperature change, made to increase the standard pressure coking time of approximately 50 hours to approximately 100 hours, was not effective in eliminating the macrocracks.

Scouting studies will be continued using combinations of diluent changes, binder level changes, and other process procedures in an endeavor to reduce the macrocracks to a minimum level.

LIQUID IMPREGNATION OF GRAPHITES

Different types of experimental graphites have been molded in the graphite fuel element development program to obtain data on carbon fillers and binders and to characterize the physical properties. The as-molded graphites range structurally from near isotropic to anisotropic. The open porosities are generally 16 to 20 percent and have variable bulk densities which are dependent on the filler, binder, and other process conditions. A general density range of 1.60 to 1.80 gms/cc is typical of most of the as-molded pieces. Physical properties are collected in this state.

It is desirable to obtain physical properties on graphites having higher densities to establish the effect of densification. Studies, now in progress, are utilizing a polymer of CAI which has been found to be an effective impregnant for graphite bodies. This section defines the current procedure being employed in these studies.

Different types of experimental graphites were liquid impregnated with a polymer of CAI prepared from CAI which contains less than 500 ppm of potassium. This polymer produces a well-graphitized "soft" carbon structure. The polymer, made by pressure heating CAI at 300° C and 300 to 800 psi for two to six hours, has a softening point at about 55° C; it produces a nominal 50 to 55 percent carbon yield when heated in an open boat to 2,200° C.

The experimental graphites are prepared by mixing a filler and binder, and molding the mixture at 1,400° C and 1,600 psi. The pieces are generally heat treated up to 2,800° C without pressure prior to impregnation. However, future work will be directed toward impregnation of the 1,400° C baked graphites. The experimental fillers range from isotropic to anisotropic carbons. In almost all cases, the filler firing temperature was 1,000° C. The binders used were thermoplastic types and include isotruxene (ITX), CAI polymer, and 350 coal-tar pitch.

IMPREGNATION PROCEDURE

Liquid impregnation of the graphites was achieved by melting CAI polymer under vacuum in contact with the graphite while increasing the temperature to approximately 125° C. The vacuum operation was maintained at temperature for approximately two hours and then the system was pressurized to ambient pressure. The experimental graphite was submerged in the liquid CAI polymer during this operation. The submerged graphite and excess CAI polymer were then transferred to a second unit for pressure application.

The pressure autoclave was heated to 180° C and a pressure of 4,500 psi was applied to the polymer-graphite body for 16 hours. The amount of pressure, temperature, and hold time was arbitrarily selected. The procedure was found to be very effective in filling all of the available open pores of the graphite.

After the pressure cycle, the polymer-graphite body was transferred to a coking furnace and heated on a programmed cycle to a maximum of 850° C. The graphite was reimpregnated after the 850° C, as required. Ultimately, the graphite was fired to 2,800° C prior to obtaining physical properties.

DENSIFICATION

The degree of densification of several graphites is shown in Table A-3. These data show that the CAI polymer and procedure used effectively increased the density of a variety of graphite types. Although the final density is dependent on many variables, densities of 1.87 to 2.02 gms/cc were achieved. The carbon weight increases show that the CAI polymer essentially filled all of the open porosity during each impregnation. A carbon yield of approximately 50 percent was obtained. Each successive impregnation increased the density by about one-half of that achieved in the preceding impregnation.

Most of the impregnated graphites show the density increased in a uniform manner. However, some did exhibit irregularities in the rate of densification. In two of these cases, the irregular fill rate was due to the fact that the CAI polymer had been previously used. (The CAI polymer, as do most of the thermoplastic resins, will change in melting point and viscosity by repeated heating under vacuum at 125° C. The increased melting point and viscosity decreases the effectiveness of the polymer as an impregnant).

The other irregularities in the rates of densification were due to problems associated with the vacuum operation. In all of these cases, during evacuation, excessive air outgassing of the CAI polymer before reaching 125° C caused the material to flow from around the graphite body. The graphite was not submersed after evacuation and therefore, not fully impregnated. However, they were carbonized to 850° C prior to reimpregnation.

LIQUID IMPREGNATION OF MOLDED GRAPHITES⁽¹⁾

Graphite Number	Filler	Binder	As-Molded Density (gms/cc)	Number of Impregnations (density, gms/cc)					Final Density Fired ⁽²⁾ (gms/cc)
				1	2	3	4	5	
131	PCD-0Q	CAI	1.68	1.77	1.85	1.90	1.93	-	1.92
133	PCD-0Q	CAI	1.70	1.84	1.87	1.93	-	-	1.92
141	PCD-0Q	CAI	1.68	1.80	1.88	1.93	-	-	1.93
143	PCD-0Q	CAI	1.70	1.85	1.91	1.93	-	-	1.93
134	PCD-0Q	ITX	1.80	1.88	1.90	1.93	-	-	1.93
135	PCD-0Q	ITX	1.76	1.84	1.86	1.89	-	-	1.88
144	PCD-0Q	ITX	1.79	1.86	1.89	1.93	-	-	1.93
170	PCD-0Q	ITX	1.79	1.81	1.87	1.88	1.91	-	1.91
171 ⁽³⁾	PCD-0Q	ITX	1.66	1.74	1.77	1.77	1.77	-	1.91
163	PCD-0Q	350 Pitch ⁽⁴⁾	1.82	1.89	1.93	1.94	-	-	1.94
147	PCD-0Q + 1% Rayon Fibers	ITX	1.82	1.93	1.95	1.96	-	-	1.96
148	PCD-0Q + 1% Phenolic Fibers	ITX	1.83	1.93	1.98	2.00	-	-	1.99
169	PCD-9 (900° C fired powder)	ITX	1.76	1.84	1.85	1.91	1.94	1.94	1.94
140	ITX	ITX	1.87	1.96	1.99	2.02	-	-	2.02
156	ITX	ITX	1.86	1.94	1.98	2.00	-	-	2.00
162	ITX	ITX	1.86	1.94	1.99	2.00	-	-	1.99
150	CAI (~ 300 ppm K)	ITX	1.74	1.83	1.90	1.94	-	-	1.94
152	CAI (~ 300 ppm K)	ITX	1.73	1.82	1.89	1.90	1.92	-	1.91
157	CAI (~ 300 ppm K)	ITX	1.69	1.80	1.87	1.93	-	-	1.92
167	CAI (~ 300 ppm K)	ITX	1.67	1.78	1.79	1.87	1.91	1.92	1.91
154	CAI (~ 300 ppm K)	CAI	1.60	1.76	1.84	1.85	1.87	1.88	1.87
155	CAI (~ 300 ppm K)	CAI	1.61	1.75	1.84	1.89	1.93	-	1.93
158	CAI (~ 300 ppm K)	CAI	1.58	1.75	1.82	1.88	1.90	1.91	1.91

(1) All graphites molded at 1,400° C and 1,600 psi using 25 pph of binder except where noted. The graphites were fired to 2,800° C, without pressure, before impregnation except for Number 171. All fillers were low-fired carbons (1,000° C) except for Number 169.

(2) Temperature at 2,800° C.

(3) Not fired to 2,800° C prior to impregnation.

(4) 35 pph of binder.

Physical properties of the nonimpregnated and impregnated graphites are shown in the "Molded Graphite" section of this report. All graphites were fired to 2,800° C before impregnation except Number 171.

MOLDED GRAPHITE STUDIES

Experimental graphites were molded and impregnated to produce specimens having a nominal 3-inch diameter and 2.5-inch length for use in studying various filler carbons and binders and to obtain physical property data. Low-fired carbons used as fillers included PCD-00, GL 1076, ITX, and two types of CAI. Binders employed included ITX, CAI, and Grade 350 coal-tar pitch. The physical properties on both the as-made and impregnated graphites were determined.

In most cases, the impregnated pieces showed a slight decrease in the isotropic properties. The strongest material produced during this report period was an impregnated isotropic graphite (Number 148), which had a flexural strength of 9,200 psi (with grain direction), a modulus of 1.6×10^6 psi (with grain), and strain at rupture of 7,300 microinches (with grain) and a CTE value of 7.2×10^{-6} in/in/°C (with grain, 25 - 1,000°C range).

As part of the graphite fuel-element development program, molded graphites are made to obtain physical property data on different carbon fillers. Several of these materials were liquid impregnated with CAI polymer to obtain data on the effect of this operation. All impregnated graphites were pre-fired to 2,800° C prior to impregnation. (Future work will study the effect of impregnation on as-made material, 1,400° C. The filler, binder, and impregnant will be graphitized in a single operation in these future studies.) The physical properties of the graphites are tabulated in Table A-4. Impregnated and nonimpregnated graphites are shown in Figures A-1 and A-2.

DENSITY

The bulk density was dependent on the type of filler and binder used in the manufacturing process. In general, densities of 1.76 to 1.88 gms/cc were obtained in the molded state. Densities of 1.91 to 2.02 gms/cc were obtained for graphites that had been liquid impregnated.

POROSITY

All of the graphites were prepared using a graphitizable resin binder and therefore, an open porosity of 17 to 22 percent was obtained. The average pore entrance diameter was small, usually less than two microns. The impregnated pieces had reduced open porosities (~ 10%) and reduced

pore entrance diameters. Typical mercury porosimetry data are shown in Table A-5.

ELECTRICAL RESISTANCE

Considerable variation in the electrical resistance can be expected since the type of carbon filler and binder was varied in these studies. The effect of impregnation on the resistivity is consistent in as much as the resistivity decreased in all cases when the density was raised by impregnation. The extent of the decrease, however, as a function of the degree of densification is not comparable for all of the graphites. The electrical resistance data can be used as a very accurate method of determining the degree of isotropy and agrees very well with BAF data obtained by X-ray techniques. It is an accurate and an inexpensive test for this property.

COEFFICIENT OF THERMAL EXPANSION

All of the fillers studied during this report period produced high CTE graphites with values ranging up to a maximum of 7.4×10^{-6} in/in/°C (25 to 1,000° C range). The CTE values are primarily related to the filler carbon. Essentially, no change was detected that could be attributed to the three binders used in these studies. The three binders, however, were selected and the carbon derived from each of the binders are about the same type, ie, well-graphitized carbon. The use of other binders could produce a change in the CTE values but they would probably not be increased to any substantial amount and may be decreased if a glassy-type carbon was used.

The effect of the impregnation on the CTE values appeared to be small but consistent. A slight decrease was noted in almost all cases but the impregnant was also selected and is a very crystalline, anisotropic carbon structure.

ISOTROPY

Most of the graphites produced a nearly isotropic body (~ 1.03 typical). Impregnation with CAI polymer produced a small effect on the anisotropy of the near isotropic graphites. The graphites become slightly anisotropic, when impregnated, which is consistent with the CTE data. The few anisotropic graphites showed a large increase in anisotropy after impregnation. The isotropic values were determined by electrical resistance ratio data and by X-ray diffraction data. Physical property data were measured in both directions (Table A-4) and the isotropic value can also be established from these data.

Table A-4
PHYSICAL PROPERTIES OF EXPERIMENTAL GRAPHITES

Graphite Number	Filler ⁽¹⁾	Binder	Impregnated	Density (gms/cc)		Accessible Porosity (%)	Average Pore Diameter (μ)	Flexural Strength (psi)	
				Bulk	Liquid			WG	AG
<u>PCD-0Q</u>									
130	PCD-0Q	CAI	No	1.70	2.17	21.9	1.2	3,800	4,400
131	PCD-0Q	CAI	Yes	1.91	2.18	12.8	1.0	5,100	5,700
143	PCD-0Q	CAI	Yes	1.91	2.18	13.0	1.0	4,700	4,600
132	PCD-0Q	ITX	No	1.78	2.14	17.4	2.0	6,100	5,900
135	PCD-0Q	ITX	Yes	1.87	2.15	13.7	1.2	5,000	5,300
<u>Fiber Addition</u>									
166 ⁽⁴⁾	PCD-0Q + 4% Rayon	ITX	No	1.80	2.16	17.2	2.6	6,300	4,600
146	PCD-0Q + 1% Rayon	ITX	No	1.80	2.14	17.3	1.1	7,800	8,000
149	PCD-0Q + 1% Phenolic	ITX	No	1.83	2.15	15.1	1.6	6,400	6,500
148	PCD-0Q + 1% Phenolic	ITX	Yes	1.99	2.13	6.3	1.2	9,200	7,900
<u>350 Coal-Tar Pitch</u>									
161 ⁽⁴⁾	PCD-0Q	350 Pitch	No	1.79	2.11	15.9	1.0	6,300	6,200
163 ⁽⁵⁾	PCD-0Q	350 Pitch	Yes	1.92	2.12	9.7	0.8	7,400	6,800
<u>PCD-9 (900° C fired)</u>									
168	PCD-9	ITX	No	1.76	2.16	18.8	2.2	5,100	4,600
169 ⁽⁴⁾	PCD-9	ITX	Yes	-	-	-	-	-	-
<u>CAI Carbon</u>									
151	CAI (< 300 ppm K)	ITX	No	1.73	2.22	22.1	1.3	3,800	3,200
152	CAI (< 300 ppm K)	ITX	Yes	1.91	2.20	13.0	0.9	5,700	4,600
153	CAI (< 300 ppm K)	CAI	No	1.58	2.26	30.9	1.2	1,700	1,500
158	CAI (< 300 ppm K)	CAI	Yes	1.90	2.21	14.7	1.2	4,100	3,200
165	CAI (2,900 ppm K)	ITX	No	1.82	2.17	16.1	0.7	5,100	5,100
<u>ITX Carbon</u>									
138	ITX	ITX	No	1.88	2.20	14.0	1.3	4,600	4,000
162	ITX	ITX	Yes	1.99	2.19	9.6	1.8	4,800	4,400
<u>GLC 1076 (1,000° C)</u>									
164	GLC 1076	ITX	No	1.71	2.17	22.8	2.9	4,400	4,900
<u>Commercial JA-5</u>									
	JA-5, As Received	-	-	1.56	2.16	28.3	8.5	4,800	4,900
<u>Commercial ATJS</u>									
	ATJS, As Received	-	-	1.85	-	-	1.0	5,100	4,500

- (1) All fillers were low-fired carbons (1,000° C) except where noted. The graphites were molded at 1,400° C and 1,600 psi using 25 pph of binder except as noted. They were fired without pressure to 2,800° C. All were impregnated with CAI polymer after the 2,800° C firing temperature and were again fired to 2,800° C to graphitize the binder.
- (2) WG - with grain; AG - across grain.
- (3) Temperature - 20 to 1,000° C.
- (4) 30 pph of binder.
- (5) 35 pph of binder.

Table A-4 (Continued)
PHYSICAL PROPERTIES OF EXPERIMENTAL GRAPHITES

Graphite Number	Modulus of Elasticity (psi x 10 ⁶)		Strain at Rupture (%)		CTE ⁽³⁾ (x 10 ⁶ in/in/° C)		Electrical Resistance (μΩ-cm)			BAF (X-ray diffraction)
	WG ⁽²⁾	AG ⁽²⁾	WG	AG	WG	AG	WG	AG	Ratio	
<u>PCD-0Q</u>										
130	1.1	1.1	0.41	0.45	7.4	7.7	1,725	1,770	1.03	1.03
131	1.4	1.4	0.40	0.46	6.8	7.1	1,290	1,305	1.01	1.02
143	1.3	1.4	0.44	0.43	6.8	7.1	1,370	1,415	1.03	1.03
132	1.2	1.2	0.57	0.55	7.0	7.6	1,350	1,395	1.03	1.02
135	1.4	1.3	0.42	0.47	7.0	7.1	1,300	1,330	1.02	1.04
<u>Fiber Addition</u>										
166 ⁽⁴⁾	1.3	1.3	0.56	0.42	6.4	7.0	1,295	1,370	1.06	1.05
146	1.4	1.5	0.71	0.71	7.0	7.4	1,400	1,470	1.05	1.05
149	1.5	1.5	0.48	0.46	6.9	7.6	1,290	1,335	1.04	1.04
148	1.6	1.4	0.73	0.67	-	-	1,125	1,215	1.08	-
<u>350 Coal-Tar Pitch</u>										
161 ⁽⁴⁾	1.3	1.3	0.59	0.55	7.2	7.6	1,340	1,360	1.02	1.03
163 ⁽⁵⁾	1.5	1.6	0.60	0.56	-	-	1,175	1,275	1.09	-
<u>PCD-9 (900° C fired)</u>										
168	1.3	1.2	0.51	0.46	-	-	1,460	1,510	1.03	-
169	-	-	-	-	-	-	-	-	-	-
<u>CAI Carbon</u>										
151	1.3	0.9	0.37	0.47	5.2	7.5	1,170	1,750	1.49	1.36
152	1.4	1.1	0.49	0.62	-	-	940	1,560	1.66	-
153	0.9	0.8	0.26	0.27	5.6	7.0	1,870	2,295	1.22	1.19
158	1.5	1.2	0.39	0.43	-	-	1,105	1,560	1.40	-
165	1.3	1.3	0.47	0.47	6.8	7.1	1,505	1,600	1.07	1.09
<u>ITX Carbon</u>										
138	1.5	1.4	0.42	0.39	6.7	8.0	1,110	1,245	1.12	1.09
162	1.4	1.3	0.45	0.47	-	-	970	1,135	1.17	-
<u>GLC 1076 (1,000° C)</u>										
164	1.0	1.1	0.55	0.59	6.6	7.6	1,400	1,380	0.99	1.04
<u>Commercial JA-5</u>										
	1.0	1.1	0.62	0.58	7.2	7.3	1,290	1,305	1.01	1.03
<u>Commercial ATJS</u>										
	1.7	1.3	0.38	0.48	3.8	4.7	840	1,095	1.30	1.23

- (1) All fillers were low-fired carbons (1,000° C) except where noted. The graphites were molded at 1,400° C and 1,600 psi using 25 pph of binder except as noted. They were fired without pressure to 2,800° C. All were impregnated with CAI polymer after the 2,800° C firing temperature and were again fired to 2,800° C to graphitize the binder.
- (2) WG - with grain; AG - across grain.
- (3) Temperature - 20 to 1,000° C.
- (4) 30 pph of binder.
- (5) 35 pph of binder.

H495-7

(a) PCD-9 Filler and ITX Binder; Density, 1.76 gms/cc.

H359-2

(b) GLC 1076 Filler and ITX Binder; Density, 1.71 gms/cc.

H359-3

(c) CAI Filler (2,900 ppm K) ITX Binder; Density, 1.82 gms/cc.

Figure A-1. NONIMPREGNATED EXPERIMENTAL GRAPHITES. (250X)

H495-4

(a) CAI Filler (< 300 ppm K), CAI Binder, and CAI Impregnant; Density, 1.90 gms/cc.

H495-5

(b) ITX Filler, ITX Binder, and CAI Impregnant; Density, 1.99 gms/cc.

H495-6

(c) PCD-0Q Filler, 350 Coal-Tar Pitch, and CAI Impregnant; Density, 1.92 gms/cc.

Figure A-2. IMPREGNATED EXPERIMENTAL GRAPHITES. (250X)

Table A-5
POROSITY DATA OF TYPICAL GRAPHITES

Graphite Number	Filler	Binder	Density (gms/cc)		Accessible Porosity (%)	Average Pore Diameter (μ)
			Bulk	Liquid		
<u>As-Molded Graphites</u>						
130	PCD-0Q	CAI	1.70	2.17	21.9	1.2
132	PCD-0Q	ITX	1.78	2.14	17.4	2.0
146	PCD-0Q + 1% Rayon Fibers	ITX	1.80	2.14	17.3	1.1
149	PCD-0Q + 1% Phenolic Fibers	ITX	1.83	2.15	15.1	1.6
161	PCD-0Q	350 Pitch	1.79	2.11	15.9	1.0
151	CAI	ITX	1.73	2.22	22.1	1.3
153	CAI	CAI	1.58	2.26	30.9	1.2
138	ITX	ITX	1.88	2.20	14.0	1.3
<u>Impregnated Graphites</u>						
131	PCD-0Q	CAI	1.91	2.18	12.8	1.0
135	PCD-0Q	ITX	1.87	2.15	13.7	1.2
148	PCD-0Q + 1% Phenolic Fibers	ITX	1.99	2.13	6.3	1.2
163	PCD-0Q	350 Pitch	1.92	2.12	9.7	0.8
152	CAI	ITX	1.91	2.20	13.0	0.9
158	CAI	CAI	1.90	2.21	14.7	1.2
162	ITX	ITX	1.99	2.19	9.6	1.8

FLEXURAL STRENGTH

The most variable property found in these studies was the flexural strength. In general, flexural strengths of 3,000 to 5,000 psi were obtained on isotropic graphites in the as-molded state. Liquid impregnation was performed on graphitized pieces and produced inconsistent results. The strength of a graphite made with PCD-0Q filler and ITX binder was not changed by densification. The same filler (PCD-0Q) bound with CAI showed an increased flexural strength when densified. The strength of a graphite made with ITX filler and ITX binder was not changed by densification. But, a CAI filler bound with CAI increased in strength when densified.

Densification of graphites prepared from PCD-0Q filler and 350 coal-tar pitch showed an increased flexural strength. The highest strength graphite

was made using PCD-0Q filler, one percent phenolic fibers, and ITX binder. When densified, this graphite had a with-grain flexural strength of 9,200 psi.

Typical flexural strength data of impregnated and nonimpregnated graphites are shown in Table A-4.

MODULUS

Typical modulus values for the graphites range from 0.9 to 1.6×10^6 psi and is dependent on the filler, density, binder, and other variables. In all cases, high-density graphites (+ 1.95 gms/cc) were prepared having modulus values of less than 1.6×10^6 psi. These data are reported in Table A-4.

STRAIN AT RUPTURE

The percent strain at rupture for the graphites was measured; the data are shown in Table A-4. Except for one graphite, all values ranged from 3,700 to 7,300 $\mu\text{in/in}$. All measurements were made by strain-gage techniques on the flexural sample at room temperature.

GLC 1076 FLOUR

Data included in Table A-4 for the graphite molded from low-fired GLC 1076 flour (Number 164) show that this graphite has a slightly lower density, flexural strength, and modulus than does a graphite fabricated from PCD-0Q flour (Number 132). The other properties, including the CTE, are essentially the same as the PCD-0Q graphite.

COMMERCIAL JA-5 GRAPHITE

This material, received in bulk form (Airco Speer Carbon-Graphite, Niagara Falls), has a low-bulk density and is nearly isotropic. The graphite has good strength and low electrical resistivity. The modulus is low and the strain at rupture is high. The property data is shown in Table A-4.

COMMERCIAL ATJS

This material (Carbon Products Division, Union Carbide Corporation) was selected because of its excellent thermal shock properties. The material was characterized using the same procedure as used for the experimental graphites. The properties noted in Table A-4 show the material to be anisotropic; a density of 1.85 gms/cc was measured on the test specimens. The strength was 5,100 psi (with grain), and a modulus of 1.7×10^6 psi

was measured. The strain at rupture was 3,800 $\mu\text{in/in}$ (with grain direction).

THERMAL SHOCK

No data on the experimental graphites are available at this time. Wafers having a thickness of 0.100 ± 0.001 inch and a diameter of 0.750 inch have been prepared for thermal shock test using the ORNL type test.

MICROSTRUCTURE OF GRAPHITES

The microstructure of all experimental graphites was examined using standard metallographic techniques. Six typical photographs representing both impregnated and nonimpregnated graphites are shown in Figures A-1 and A-2.

VAPOR-COATED ZIRCONIUM CARBIDE TUBES—THICK-WALLED CYLINDERS

During this report period, tubes of zirconium carbide were made, and chemical analyses of the deposited coatings were obtained. Tubes were submitted to LASL for the determination of the CTE.

The endeavor to fabricate and obtain physical properties of vapor-deposited tubes of zirconium carbide has been continued. Data obtained from previous work⁽¹⁾ had shown that thick-walled tubes could be produced at plating temperatures comparable to the ones used in coating of fuel elements. The initial studies were primarily concentrated toward obtaining data on niobium carbide, and consequently, only a limited amount of data on zirconium carbide was obtained. The primary goal of the present study is to obtain the coefficient of thermal expansion of vapor-deposited ZrC tubes.

Additional runs have been made to produce thick-walled vapor-deposited cylinders of GEM ZrC. A previous run⁽¹⁾ had produced various properties but additional data were needed. One of the primary goals of this study was to obtain the thermal expansion (CTE) of coatings deposited at fuel-element coating temperatures (1,100 to 1,150° C).

COATING PROCEDURE

A central support element having an inside hole diameter of 0.53 inch was first coated with a thin (~ 1.5 mils) layer of pyrocarbon to reduce the adherence of the coating to the element and to facilitate the removal of the ZrC cylinders without cracking. The ZrC run was made at a temperature span of 1,125 to 1,310° C. These are higher temperatures than the previous run (1,050 to 1,250° C) which was made in 1970 and was chosen in order to produce thick-walled tubes which were equivalent to the cold-end temperature of fuel elements (~ 1,150° C). However, the run was prematurely terminated after 53 hours due to solids buildup in the exit line. The deposition conditions and resulting thickness profile are shown in Figure A-3. A 13-inch long tube (39- to 52-inch location) was obtained intact with a wall thickness of 20 to 47 mils. However, at the desired cold-end region, the short run time produced a thickness of less than 20 mils and the tubes cracked upon removal from the mandrel. Chemical analyses were taken on the cracked pieces and are shown in Table A-6.

Date	Run	Type	Run Time	Weight Gain (%)				Pre-Heater	Number and Type Elements	Gas Flow (l/m/e)					Salt (g/m e)
				High	Low	Average	Gms/Hr			Argon	HCl	H ₂	CH ₄	Salt	
8-2-71	568	ZrC	53	128.4	127.8	128.1	2.42	14	Thick 2 Tubes	9.0	-	0.180	0.040	0.188	1.82

Figure A-3. THICK-WALLED CYLINDERS OF GEM-ZrC.

However, the CTE and other physical properties data can only be taken from the free-standing tubes. Additional runs are planned to produce the thick tubes at the cold-end region of the element.

CARBON-ZIRCONIUM CONTENT AND CARBON-TO-ZIRCONIUM RATIO

Table A-6 shows the total carbon, free carbon (combined carbon by difference) and zirconium content of the coatings at varying deposition temperatures. All contents were determined by chemical analysis. Although there is some variability in the data (especially the free carbon), the carbon, zirconium, and thus the carbon-to-zirconium ratio increased as the deposition temperature increased along the element length. The free-carbon content is believed to be biased high in the samples taken at Element Position 16. The high result could be contamination of carbon adhering to the surface of the coating. The combined carbon-to-zirconium ratio is shown in Figure A-4 as a function of the deposition temperature.

Table A-6
PROPERTIES OF GEM-ZrC THICK-WALLED CYLINDERS

	Deposition Temperature ($^{\circ}$ C)						
	1,075	1,125	1,150	1,200	1,225	1,265	1,300
Element Position (in)	5	10	16	30	37.5	45.5	51.5
Chemical Analysis-							
Carbon (%)							
Total	8.493	8.754	8.684	10.078	10.156	10.744	10.850
Free	0.055	0.056	0.297 ⁽¹⁾	0	0.054	0.040	0
Combined	8.438	8.698	8.387	10.078	10.144	10.704	10.850
Zirconium (%)	85.16	85.09	86.13	83.79 ⁽¹⁾	86.43	86.64	87.99
Combined C/Zr Ratio	0.752	0.776	0.739 ⁽¹⁾	0.913 ⁽¹⁾	0.892	0.938	0.937
X-Ray Diffraction							
Major Phase	ZrC	ZrC	ZrC	ZrC	ZrC	ZrC	ZrC
Minor Phase	ZrO ₂	ZrO ₂	ZrO ₂	ZrO ₂	ZrO ₂	None	None
Lattice Parameter (Å)	(2)	(2)	(2)	(2)	(2)	(2)	4.6943 ⁽¹⁾
Chlorine Content (%)	1.204	0.909	0.689	0.634	0.609	0.213	0.106
Oxygen Content (%)	3.69	3.27	2.81	1.97	1.35	0.77	0.41
Metallic Impurities (ppm)							
Al	80	60	50	60	50	75	2
Fe	500	300	300	175	100	50	30
Si	600	400	300	600	400	300	< 10

(1) Value questionable, not consistent with other data (see text).

(2) X-ray pattern very wide and diffuse, probably due to impurity level.

Figure A-4. CARBON-TO-ZIRCONIUM RATIO OF GEM-ZrC THICK-WALLED CYLINDERS.

PROPERTIES

X-Ray Diffraction

The X-ray diffraction analysis was hindered by the concentration of oxygen and chlorine. The patterns were wide and diffuse; the lattice parameters were determined for only the sample taken at the very hot end where the combined oxygen and chlorine content was approximately 0.5 percent. Even at this level, the lattice parameter value was not compatible with the carbon-to-zirconium ratio determined by chemical analysis. A secondary zirconium oxide phase was detectable in some samples ($> 1.35\%$ oxygen samples).

Chlorine Content

The chlorine content of this ZrC run was lower by a factor of three than the previous run. The chlorine content, as a function of the deposition temperature, is shown in Figure A-5. The lower chlorine content was probably a result of the high deposition temperature.

Figure A-5. IMPURITY LEVEL OF GEM-ZrC THICK-WALLED CYLINDERS.

Oxygen Content

Although made at high temperatures, the oxygen content of this run was about the same as the previous run. This oxygen content is also shown in Figure A-5. This high oxygen content may be partially due to the fact that some of the process lines were contaminated with butadiene used in the impregnation studies. The gas lines have been cleaned and other process improvements made in an effort to eliminate this impurity.

Metallic Impurities

As shown in Table A-6, the only significant metallic impurities present were aluminum, iron, and silicon and these were less than 600 ppm for each impurity. As with the other impurities, the concentration tended to decrease as the temperature increased along the element length.

Coefficient of Thermal Expansion (CTE)

The intact portion of the ZrC tube had a nominal length of 13 inches. This section represented the region between 39 to 52 inches and had a plating temperature span of 1,235 to 1,300° C. The N-1 Group, LASL, agreed to obtain the coefficient of thermal expansion, shrinkage, and other thermal stability data on sections five inches in length. The intact tube was sampled on each end and in the center for metallographic analysis (Figure A-6) and chemical analysis. The remaining sections were cut into two 5-inch length tubes and each tube had two fiducial holes drilled at the required locations. Two additional sister ZrC tubes are being held as potential recheck samples.

At this time, the CTE values are not yet available. The chemical analysis and other related data on the tubes can be obtained from Table A-6 and are represented by the element position samples taken at 37.5, 45.5, and 51.5 inches.

Metallographic Examination

Specimens from each sample location were examined using metallographic techniques. The structure of the tubes was of fine-grained crystals. The crystal sizes increased with increased plating temperatures. Typical

(a) Sample Location 45 1/2 Inches.

MS-71-0759-1

(b) Sample Location 51 1/2 Inches.

MS-71-0759-2

Figure A-6. VAPOR-DEPOSITED TUBES OF ZrC. (100X)

photographs of two areas of the tube (45 1/2 and 51 1/2 inch zones) are shown in Figure A-6. These samples were taken at the point where the CTE samples were selected.

GEM-ZrC BORE COATINGS

Coating studies have continued in which films of zirconium carbide were deposited in fuel element bores. During this report period, coating temperatures were raised and the chemical purity of the coatings was improved. Most of the experimental runs were made to obtain ZrC profile distribution data and analysis of the deposited coatings. Hot gas test elements were also coated and the results are reported in the "Hot Gas Test Evaluation" section of this report.

The purity of the higher plating temperature coatings are improved, and the hot gas test data, although limited, appears to be improved. The cracks in the ZrC coatings, determined by high-resolution, eddy-current inspection (HREC) were reduced by the increased plating temperatures.

Earlier coating studies have shown a lower level of impurities in ZrC coatings when deposited at higher temperatures. Several experimental coating runs were made to arrive at various ZrC profiles. The nominal coating conditions and chlorine content for these runs are shown in Table A-7. Run 83020Q was the typical coating used for the recent testing of POCO LF elements as Generations 3 and 4. The coating gas composition was changed (lower hydrogen, lower methane), and the temperatures were raised for Run 83024Q. POCO LF elements from this run were tested as Generation 6. Temperatures were raised further in Run 83026Q which produced a faster coating rate and a more uniform coating distribution. For comparison, the temperature gradients used for two of the runs are shown in Figure A-7 and the resulting coating profiles are shown in Figure A-8.

CHLORINE CONTENTS IN BORE COATINGS

The chlorine content of the GEM-ZrC coatings decreased as the coating temperatures were increased. Figure A-9 shows the chlorine content along the element length for elements coated in Run 83016Q (same conditions as Run 83020Q) as compared to the content of elements coated at the higher temperatures used in Run 830206Q. There is some scatter in the data for Run 83026Q but the general lower level is evident.

HIGH-RESOLUTION, EDDY-CURRENT (HREC) GAGE

With the installation of a HREC gage in the plant, additional information concerning the coating cracks were obtained. After using the gage for a period of time, it became apparent that different elements in the same

Figure A-7. VARIOUS GEM-ZrC DEPOSITION TEMPERATURE GRADIENTS.

Figure A-8. VARIOUS GEM-ZrC COATING THICKNESS PROFILES.

coating batch gave somewhat varying coating crack traces. This led to the question of the matrix effect on the data. An uncoated element with an obvious longitudinal crack was run on the normal eddy-current gage and the flaw, located between 14 and 18 inches, was detected. This is shown in Figure A-10(a). When the bore was run on the HREC gage in the normal position (A flat up), the defect did not show up as shown in Figure A-10(b). However, when the element was rotated one flat (F flat up), the defect was detected as shown in Figure A-10(c). Thus it appears

Figure A-9. CHLORINE CONTENT OF VARIOUS GEM-ZrC COATING.

Figure A-10. HREC DATA—ROTATED ONE FLAT. (Element 500-300527, Bore 16)

that if the HREC window (sensing unit) of the HREC probe is looking at a matrix defect, it will affect the HREC data.

Also, a coated element was run on the HREC gage and the trace is shown in Figure A-11(a). Then the element was manually flexed to simulate what could happen with rough handling and then the element was rerun. The HREC trace showed the increase in coating cracks as shown in Figure A-11(b).

Figure A-11. HREC DATA. (Element 500613, Bore 7; Coating Run 83025)

The HREC data for the three bore coating runs made at the varying conditions (Table A-7) are shown in Figures A-12 through A-14. Figure A-12 shows POCO LF elements (tested as Generation 4) from coating Run 83020Q. Figure A-13 shows POCO LF elements (tested as Generation 6) from Coating Run 83024Q. These were elements having the first temperature increase and lower hydrogen and methane flows. The amount of cracking at the cold end appears reduced but not at the hot end. The temperatures were further increased in Run 83026Q, and Figure A-14 shows that the POCO LF elements have essentially no cracks from 0 to 20 inches, very few cracks from 20 to 40 inches, but still a fair number from 40 to 52 inches.

HREC data were also taken for elements coated, Run 83026Q, but of matrices which had lower CTE values; Figure A-15 shows a Santa Maria coke element and Figure A-16 shows a GL-1008 element. The great difference in the coating cracks for the lower CTE elements are quite evident.

Table A-7
GEM-ZrC COATING PARAMETERS

	Coating Run		
	83020Q	83024Q	83026Q
Gas Composition (l/min/element)			
Argon	2.0	2.5	2.5
Hydrogen	0.59	0.33	0.33
Methane	0.038	0.020	0.020
ZrCl ₄	0.058	0.062	0.063
Run Time (hrs)	33	30	30
Coating Weight (gms)	101.6	109.1	128.1
Coating Rate (gms/hr)	3.08	3.64	4.27
Coating Temperature (° C)	1,075 - 1,240	1,110 - 1,370	1,120 - 1,400
Chlorine Content of Coating (ppm)	~ 20,000 to 1,000	Not Sampled	~ 10,000 to 100

Figure A-12. HREC DATA RUN 83020Q, POCO LF ELEMENTS - BORE 7.

Figure A-13. HREC DATA RUN 83024Q, POCO LF ELEMENTS - BORE 7.

Figure A-14. HREC DATA RUN 83026Q, POCO LF ELEMENTS - BORE 7.

Figure A-15. HREC DATA RUN 83026Q, SANTA MARIA COKE ELEMENTS - BORE 7.

Figure A-16. HREC DATA RUN 83026Q, GL-1008 ELEMENTS - BORE 7.

In summary, it was found that matrix cracks prior to bore coating may or may not be detected by the HREC instrument. Higher plating temperatures will result in fewer coating cracks on high CTE matrices. Rough handling of essentially crack-free coatings will result in detectable cracked coatings. A run in which three matrix types were coated (low, medium, and high CTE) resulted in detectable crack differences by the HREC data.

HOT GAS TEST EVALUATION

Several bead-loaded graphite fuel elements, coated with GEM ZrC, were electrically hot gas tested at both WANL and LASL. The elements, tested by WANL, were defined as Generations 3 and 4. The WANL results were similar to the LASL test results. The elements showed a high carbon loss region in the 20- to 30-inch area. It is believed that the matrix quality of the elements were poor; also, the coatings contained a high level of chlorine impurity.

Elements defined as Generations 5 and 6 were tested at LASL. The Generation 5 elements were coated elements remaining from Generations 3 and 4 but were heat treated to stabilize the coating. A thin recoat was applied to the bores. No significant improvement in performance was detectable. The Generation 6 elements were coated with a process which produced a reduced level of chlorine contamination. The matrix quality was also poor. However, the hot gas test performance was improved. The losses at the 20- to 30-inch region was significantly lower than previous elements.

WANL TESTING

Three POCO LF elements (Generations 3 and 4) were hot gas tested at WANL. Sister elements were tested previously at LASL and the data have been reported.⁽²⁾ The before coating matrix quality (based on eddy current) was not good and the HREC data showed coating cracks from about 0 to 30 inches. A summary of the test results is presented in Table A-8. In general, the data are similar to the LASL results; the 25- to 30-inch region was sensitive to cyclic testing. The coating conditions and profile for these elements are shown in Figure A-17. The MULE data for the three elements are shown in Figures A-18 through A-20.

LASL TESTING

Since bore coatings, deposited at higher temperatures, produced the lower level of impurities, the elements from Generations 3 and 4 were reprocessed in an attempt to stabilize the coating and reduce the impurity level of the GEM ZrC bore coating. These elements were defined as Generation 5. The treatment given these elements are defined in the Generation 5 section of this report but the hot gas test performance was not improved. The last group of experimental POCO LF elements were given a single GEM-ZrC coating of a low chlorine content and was defined as Generation 6. In testing these Generation 6 elements, the mid-band loss did not occur in the normal 20- to 30-inch region but a slight amount occurred at the 8- to 18-inch region. A summary of the LASL testing is shown in Table A-8.

Table A-8
HOT GAS TEST SUMMARY - POCO LF MATRIX

Generation	Element	Bore Coating Run	Type Test	Test Temperature (° R)	Total Time (min)	Number of Cycles	Weight Loss (gms)		
							0-35"	35-50"	0-50"
WANL									
3	500-300506 ⁽¹⁾	83020Q ⁽²⁾	E02/E04 ⁽³⁾	-	39.5	4	2.7	0.1	2.8
4	500-300555	83020Q	E02/E04	-	47.5	5	5.8	2.1	7.9
4	500-300568	83020Q	E02/E04	-	60.1	7	2.7	3.8	6.5
LASL									
5	500-300477	83018Q ⁽⁴⁾ + 83023Q	-	4,000	50	5	NA	NA	3.5
5	500-300533	83020Q ⁽⁴⁾ + 83023Q	-	4,000	96	10	2.4	1.2	3.6
6	500-300608	83024Q	-	4,000	170	17	0.9	6.2	7.1

(1) Gaseous impregnated after graphitization

(2) Outside diameter surfaces coated in Run 81020Q.

(3) WANL lower power test (~ 780 kw) intended to be comparable to LASL 4,000° R.

(4) Elements were heat treated at 2,225° C (observed temperature) between the two runs.

Date	Run	Type	Run Time	Weight Gain (%)				Pre-Heater	Number and Type Elements	Gas Flow (l/m/e)					Salt (g/m/e)
				High	Low	Average	Gms/Hr			Argon	HCl	H ₂	CH ₄	Salt	
3-15-71	83020Q	OD GEM ZrC	20	21.8	19.2	20.5	1.02	59	14 POCO LF-3	2.0	-	0.59	0.038	0.052	0.51
3-18-71	83020Q	ID GEM ZrC	33	106.4	95.7	101.6	3.08	102	14 POCO LF-3	2.0	-	0.59	0.038	0.058	0.55

Figure A-17. COATING CONDITIONS - WANL TESTED GENERATIONS 3 AND 4.

Test	Element	Matrix	Test	Cycles x Minutes	Total Weight Loss		0 - 35		35 - 52		Comments
					Gross	Correct	pH	Weight	pH	Weight	
Gen. 3	500-300506	IMP POCO LF-3	WANL E02/E04	3 x 10 + 91/2	3.2	2.8	6	267	-	0.14	Broke at 26"; Cracks at 8 1/2 and 21 - 26"

Figure A-18. WANL TEST DATA - GENERATION 3, POCO LF ELEMENT 500-300506.

Test	Element	Matrix	Test	Cycles x Minutes	Total Weight Loss		0 - 35		35 - 52		Comments
					Gross	Correct	pH	Weight	pH	Weight	
	500-300555	Not IMP POCO LF-3	WANL E02/E04	4 x 10 + 7 1/2	9.5	8.0	25	5.77	-	2.11	Broke at 28"

Figure A-19. WANL TEST DATA - GENERATION 4, POCO LF ELEMENT 500-300555.

Test	Element	Matrix	Test	Cycles x Minutes	Total Weight Loss		0 - 35		35 - 52		Comments
					Gross	Correct	pH	Weight	pH	Weight	
	500-300568	Not IMP POCO LF-3	WANL E02/E04	6 x 10 + 0.1	9.5	6.9	-	2.72	-	3.73	Broke at "H" End Grip

Figure A-20. WANL TEST DATA - GENERATION 4, POCO LF ELEMENT 500-300568.

Generation 5 Elements

Hot-gas testing of Generation 3 and 4 elements showed the elements to be sensitive to cyclic testing. Also, the GEM-ZrC coating had a known chlorine content that varied from a high of approximately 20,000 ppm at the cold end to approximately 1,000 ppm at the hot end. It was decided to attempt to purify and stabilize the coating on nontested elements.

The elements, now labeled as Generation 5, were heat treated at 2,225° C (observed) in an argon-carbon atmosphere. The elements were then overcoated with a thin layer (~ 1 mil) of GEM-ZrC (low chlorine deposition conditions). The overcoating step also served to fill in any cracks or defects caused by the heat treat operation. As shown in Table A-8, the hot-gas test results were not materially improved. Figure A-21 shows the coating conditions and MULE data for Element 500-300533. Although the element only lost 3.5 grams in essentially 9.5 cycles, an appreciable mid-band loss was present.

Date	Run	Type	Run Time	Weight Gain (%)				Pre-Heater	Number and Type Elements	Gas Flow (l/m/e)					Salt (g m e)
				High	Low	Average	Gms/Hr			Argon	HCl	H ₂	CH ₄	Salt	
3-18-70	83020Q	GEM ZrC	33	106.4	95.7	101.6	3.08	102	14 POCO LF	2.0	-	0.59	0.038	0.058	0.55
6-7-71	83023Q	GEM ZrC	12	43.9	36.4	40.3	3.36	8	11 POCO LF	2.54	-	0.33	0.020	0.074	0.71

Test	Element	Matrix	Test	Cycles x Minutes	Total Weight Loss		0 - 35		35 - 52		Comments
					Gross	Correct	pH	Weight	pH	Weight	
	500-300533	POCO LF-3	LASL 4000	9 x 10 + 6	5.0	3.6	-	2.37	-	1.23	Broke at 25 3/4 Tip Off

Figure A-21. LASL TEST DATA - GENERATION 5.

Metallographic samples after the heat treat and overcoating runs are shown in Figure A-22. After heat treat, the base coat had large crystals and a large amount of porosity at the grain boundaries at Element Station 10 and

(a) 10 Inches.

MS-71-0602-1

(b) 27 Inches.

MS-71-0602-2

(c) 44 Inches.

MS-71-0602-3

Figure A-22. POCO LF ELEMENT 500-300534, GENERATION 5, AS-COATED. (Base Coat is Run 83020Q After Two Hours Heat Treat at 2,225° C Observed; Top Coat is Run 83020Q; 400X)

27 inches. However, at 44 inches, only about 50 percent of the base ZrC coat was affected. This is probably due to a small temperature gradient in the heat-treat furnace at 2,225° C. Metallographic samples, after hot gas testing, are shown in Figure A-23. At 15 and 35 inches, the character of the coatings apparently did not change, but at 45 inches, the coating recrystallized.

(a) 10 Inches.

MS-71-0614-7

(b) 35 Inches.

MS-71-0614-5

(c) 45 Inches.

MS-71-0614-6

Figure A-23. POCO LF ELEMENT 500-300477, GENERATION 5, AS TESTED. (Base Coat is Run 83020Q After Two Hours Heat Treat at 2,225° C Observed; Top Coat is 83023Q; 400X)

The high-resolution, eddy-current data, after bore coating, showed a rather large amount of coating cracks. Therefore, the unimpressive hot-gas test performance was not unexpected. The HREC data for both tested elements are shown in Figures A-24 and A-25.

Generation 6

The last group of POCO LF elements (Generation 6) were given a single GEM-ZrC coating. The higher deposition temperatures were used which produced lower chlorine contamination and reduced the number of coating cracks in the coating, especially at the mid-band region.

The coating conditions and MULE data are shown in Figure A-26. HREC data for a coated element before and after testing are shown in Figures A-27 and A-28. The elements were tested for 17 cycles, and had a mid-band loss of only 0.1 gm/in; the mid-band loss shifted from the normal 20- to 30-inch region to the 8- to 18-inch area. For a test of 17 cycles, this is one of the lowest mid-band losses for a graphite element. It appears that the change in the coating conditions were beneficial. It is planned to further increase the coating temperature in an endeavor to further improve the element bores.

Figure A-24. HREC DATA POCO LF ELEMENT 500-300477 GENERATION 5 - BEFORE HOT-GAS TEST, BORE 10.

Figure A-25. HREC DATA - POCO LF ELEMENT 500-300533 GENERATION 5 - BEFORE HOT-GAS TEST.

Date	Run	Type	Run Time	Weight Gain (%)				Pre-Heater	Number and Type Elements	Gas Flow (l/m ² e)					Salt (g/m ² e)
				High	Low	Average	Gms/Hr			Argon	HCl	H ₂	CH ₄	Salt	
6-10-71	81024Q	OD GEM ZrC	20	24.5	19.9	21.9	1.09	49	Generation 6 POCO LF-3	2.0	-	0.59	0.038	0.053	0.51
6-21-71	83024Q	ID GEM ZrC	30	114.5	105.6	109.1	3.64	51	Generation 6 POCO LF-3	2.5	-	0.33	0.020	0.062	0.60

Test	Element	Matrix	Test	Cycles x Minutes	Total Weight Loss		0 - 35		35 - 52		Comments
					Gross	Correct	pH	Weight	pH	Weight	
	500-300608	Generation 6 POCO LF-3	LASL 4000	17 x 10	27.2	7.1	-	0.9	-	6.2	Hot End Bruned Off (1") No Tip Lost Over Pressure

Figure A-26. LASL TEST DATA - GENERATION 6.

Figure A-27. HREC DATA - POCO LF ELEMENTS - GENERATION 6, ELEMENT 500-300608 BEFORE HOT-GAS TEST, BORE 10.

Figure A-28. HREC DATA - POCO LF ELEMENTS - GENERATION 6, ELEMENT 500-300608 AFTER HOT-GAS TEST, BORE 10.

The HREC data on the coated element showed a general reduction in the coating cracks in the mid-band area. Figure A-27 shows the HREC data for Element 500-300608 before testing and Figure A-28 shows the data after testing. The increase in crack after testing is obvious.

IMPROVED FUEL BEAD STUDIES

Fuel beads, with excellent thermal stability up to 2,800°C, have been previously made by loading ion exchange resin beads with uranium. These particles were then coked in an inert atmosphere and coated with a shell of pyrocarbon. The limiting factor in applying these fuel particles to the NERVA program has been the low uranium concentration of the beads. Development activities have continued to investigate methods designed to obtain increased uranium contents. A macroreticular-type resin has been found to be superior to the gel-type resins.

POLYSTYRENE-DIVINYLBENZENE, AMBERLITE 200

A macroreticular polystyrene-divinylbenzene sulfonated ion exchange resin was suggested as a potential candidate to obtain a higher uranium loading than the same chemical composition gel-type resin. The high surface area of the macroreticular beads produced a loaded, coked product (850° C bake state) that was prone to oxidation when exposed to ambient conditions. The same loaded particles, when heated to above 1,500° C without an air exposure, was stable under normal ambient conditions. The maximum uranium loading of these type beads, during this report period, was 55.4 percent uranium after heating to 1,600° C. Chemical analyses of these bead types are presented in Table A-9.

GEL-TYPE CATION EXCHANGE RESINS

Table A-9 shows a summary of the chemical composition of gel-type beads made during this report period. The resin labeled Dowex 50W contained eight percent cross-linkage and was further defined as Lot 35792. This material was used in an experiment designed to study the loading effect as a function of the pH of the uranium solution. Figure A-29 is a plot of the uranium concentration in coked beads as a function of the acidity of the uranium loading solution. These data show that the uranium concentration increased linearly with decreasing acid concentration. The maximum pH solution studied in this period was 3.5 which produced the highest loaded cores. Similar data for other ion-exchange resin types will be developed in future studies.

THERMAL STABILITY OF BEADS

Four samples of beads were loaded with uranium; the batch numbers were FC-112, FC-113, FC-114, and FC-119. Chemical analyses of the loaded beads are shown in Table A-9. Aliquots of each bead type were sent to

Table A-9
CHEMICAL ANALYSIS OF LOADED ION EXCHANGE RESINS

Batch Number	Loading Solution	Coking Temperature (°C)	Coke Yield (%)	Analysis (%)				O ₂	Comments
				U	C	H ₂	S		
Amberlite 200 Resin, Macroreticular Type									
FC-111	0.27 gm U/gm NO ₃ ⁻	950	66.9	-	-	-	-	-	Oxidized.
FC-111	0.27 gm U/gm NO ₃ ⁻	1,000	-	43.88	34.97	-	-	-	
FC-111	0.27 gm U/gm NO ₃ ⁻	1,600	-	55.40	38.68	-	-	1.68	Degassed at 1,600° C.
FC-112	0.27 gm U/gm NO ₃ ⁻	1,800	-	-	-	-	-	-	
FC-113	0.01 gm U/gm SO ₄ ⁻	925	72.9	43.68	34.88	0.60	4.72	-	Partially oxidized.
FC-113	0.01 gm U/gm SO ₄ ⁻	(1)	-	37.53	37.55	0.61	4.78	-	Leached in HNO ₃ -Hf.
FC-113	0.01 gm U/gm SO ₄ ⁻	1,800	63.6	53.32	36.05	0.29	4.03	-	No oxidation.
FC-115	0.01 gm U/gm SO ₄ ⁻	950	71.2	41.6	37.5	0.52	5.00	-	Loaded with a solution of pH of 1.5.
FC-115	0.01 gm U/gm SO ₄ ⁻	(2)	-	42.6	44.1	0.39	1.79	-	Leached in HNO ₃ -Hf.
Gel-Type Beads									
FC-114 ⁽³⁾	0.01 gm U/gm SO ₄ ⁻	965	71.7	47.22	37.64	0.22	7.55	-	Solution of pH of 3.0.
FC-114 ⁽³⁾	0.01 gm U/gm SO ₄ ⁻	1,000	-	45.7	38.4	0.36	9.68	0.56	Solution of pH of 3.0; coated with PyC.
FC-120 ⁽⁴⁾	0.02 gm U/gm NO ₃ ⁻	950	70.1	42.28	41.97	0	7.42	-	Solution of pH of 0.5.
FC-116 ⁽⁴⁾	0.01 gm U/gm SO ₄ ⁻	1,010	70.0	43.97	41.47	0.43	7.96	-	Solution of pH of 1.6.
FC-118 ⁽⁴⁾	0.02 gm U/gm NO ₃ ⁻	900	72.1	48.46	38.01	0.01	9.82	-	Solution of pH of 2.5.
FC-117 ⁽⁴⁾	0.02 gm U/gm NO ₃ ⁻	1,015	71.3	48.25	35.47	0.32	9.48	-	Solution of pH of 3.4.
FC-119 ⁽⁴⁾	0.02 gm U/gm NO ₃ ⁻	955	70.6	52.19	33.54	0.38	8.11	-	Solution of pH of 3.4.
FC-119-1 ⁽⁴⁾	0.02 gm U/gm NO ₃ ⁻	950	-	50.67	33.61	0.39	7.32	-	Solution of pH of 3.4.
FC-121	0.27 gm U/gm NO ₃ ⁻	950	70.2	48.67	36.72	0.51	7.84	-	Solution of pH of 3.4.

(1) Carbonized Batch FC113 acid leached to remove surface material.

(2) Carbonized Batch FC115 acid leached to remove surface material.

(3) Bead Type AGC-243.

(4) Bead Type Dowex 50W.

Figure A-29. EFFECT OF pH OF LOADING SOLUTION ON WEIGHT PERCENT URANIUM IN 1,000° C COKED RESIN BEADS.

the Oak Ridge National Laboratory and were coked and pyrocarbon coated. The coated particles were heat treated to 2,800° C for three hours; micro-radiographs of the heated beads are shown in Figure A-30. The pyrocarbon coating conditions were not optimized for these particles, especially for the FC-112 batch (small particles). Clumping of particles occurred during the pyrocarbon coating run. Since the only known difference between FC-112 and FC-113 batches was particle size, it is believed that both batches would be about equal in thermal stability if the coating parameters were equalized. In all four cases, the beads survived the three-hour heat treatment at 2,800° C.

A batch of loaded macroreticular beads (Amberlite 200) were heat treated at 2,600° C for 2 hours, 2,800° C for 2 hours, and 3,000° C for 45 minutes. The beads survived these heating cycles. Chemical analyses of the 875° C coked particles and the 1,750° C coked particles are shown in Table A-10. The loaded resin beads were processed to 100° C in air to dry the particles. The beads were further heated to 275° C in air and a loss of 9.2 percent occurred (100 to 275° C). The beads were coked to 875° C under argon, cooled, and exposed to ambient conditions. Some oxidation may have occurred due to this operation. The beads were later coked to 1,750° C, cooled, and exposed to ambient conditions. The beads were then coated with pyrocarbon, and later were heated up to 3,000° C.

The bead internal quality after heat treatment was studied by radiographic and metallographic techniques. Coated beads which were heated to 2,800° C for two hours are shown in Figure A-31. A structural change

(a) Run FC-112.

(b) Run FC-113.

(c) Run FC-114.

(d) Run FC-119.

Figure A-30. MICRORADIOGRAPHS OF HEATED BEADS. (Heat Treated at $2,800^{\circ}\text{C}$ for 3 Hours.)

(a) Run FC-104, As Coated.

(b) Run FC-104, As Coated.

(c) Run FC-104, Heat Treated at $2,800^{\circ}\text{C}$ for 2 Hours.

(d) Run FC-104, Heat Treated at $2,800^{\circ}\text{C}$ for 2 Hours.

Figure A-31. HEATED BEADS. (100X)

Table A-10
ANALYSIS OF BATCH FC104 BEADS

	Coked Particles (° C)	
	875	1,750
Resin	Amberlite 200	Amberlite 200
Mesh (as received)	+ 35	+ 35
U (%)	44.66	55.28
C (%)	35.61	37.83
H ₂ (%)	0.71	0.09
S (%)	6.12	3.55
O ₂ (%)	-	2.47
N ₂ (%)	-	0.06
Na (ppm)	240	-

is apparent in the heat-treated bead as compared to the nonheat treated bead. Some migration into the pyrocarbon occurred but no evidence of full penetration of the shell was apparent.

SYNTHESIS AND EVALUATION OF HIGH-CARBON-YIELD COMPOUNDS

Previous studies have shown that carbon precursor materials derived from indene (C_9H_8) have the ability to produce an isotropic and reproducible carbon structure. Studies made during this report period were concentrated on CAI, ITX, and other indene type compounds. Various organic compounds added to CAI have the ability to control the type of carbon which is produced from the organic resin.

PRECURSORY CARBON STUDIES

Studies of carbon precursor materials were continued in efforts to understand those factors associated with precursor properties and processing conditions that directly influence properties of derived carbon. Extension of this understanding should allow control of carbon properties which continue to be a prime goal of this endeavor. Precursor materials derived from indene, which constitute the primary materials used in these evaluations, allow considerable flexibility in the choice of polymer and carbon properties, and, thus, appear to form a precursor system which will afford controllable and reproducible carbon properties.

Preparation of Cinnamylideneindene Using Tetramethylammonium Hydroxide

Cinnamylideneindene was prepared using tetramethylammonium hydroxide (TMAH) in yield and purity that equals or surpasses that obtained using potassium hydroxide. An indene/cinnamaldehyde/TMAH molar ratio of 1.0/0.67/0.22 was found to be the most appropriate for CAI preparation in that a high purity (98%) and yield (56%) were obtained by use of a minimum amount of base. Recent efforts to optimize the preparative procedure involved the preblending of indene and cinnamaldehyde and adding the resulting mixture dropwise to a stirring solution of TMAH in methanol. After one hour's stirring, the product (54% yield) was collected by filtration and dried. Gel permeation chromatographic (GPC) analysis estimated the product to contain 9.6 percent organic impurity. Thus, preblending of indene and cinnamaldehyde appears practical but is accompanied by a slight reduction in product purity.

A similar blend of indene and cinnamaldehyde was added in one portion to a TMAH/methanol solution and allowed to stand with no stirring for one hour. The product (50% yield) contained 22 percent organic impurities, as estimated from GPC analysis. For applications which may utilize lower purity CAI, this would be a convenient preparative method.

The optimum temperature range for CAI preparation using KOH was found to be 25 to 35° C. Reaction temperatures below 15° C resulted in a very low yield (20%) of a low-purity product (41% CAI). Reaction rates at temperatures below 15° C were slow, and there was apparently no reaction at temperatures below 10° C. Reactions carried out at 5° C using TMAH instead of KOH resulted in a 38 percent yield of CAI product with 30 percent organic impurity. Though CAI can be prepared at 5° C using TMAH, optimum temperatures for maximum CAI-yield and purity are in the range 25 to 35° C.

Solubility of Cinnamylideneindene (CAI) in Various Solvents

The solubility of CAI in various organic solvents was determined at 25° C by adding ten grams CAI powder to 100 cc of the respective solvent, allowing the mixture to stir for five minutes, and subsequently, filtering and weighing the insoluble content. Resulting data are listed in Table A-11. As can be seen, the solubility of CAI is not great in any of the designated solvents though dimethylformamide appeared to be the best solvent with chlorinated methane compounds second best. The limited solubility of CAI is attributed to a high order of crystallinity of monomer molecules (melting point approximately 190° C). As a result, low molecular weight (< 1,000) polymers of CAI in general have a greater solubility than the monomer, and represent a more useful form for processing that requires dissolution of the precursor.

Table A-11
SOLUBILITY OF CINNAMYLIDENEINDENE
IN VARIOUS SOLVENTS⁽¹⁾

Sample	Solvent	Solubility ⁽²⁾ (gms/100 cc)
A	Chloroform	3.5
B	Methylene Chloride	3.4
C	Trichloroethylene	2.3
D	Perchloroethylene	0.6
E	Dimethyl Sulfoxide	1.4
F	Dimethylformamide	5.4
G	Chlorobenzene	2.3

(1) Solubilities determined by adding ten grams of CAI powder to 100 cubic centimeters of solvent (at 25° C), and weighing insolubles collected after stirring for five minutes.

(2) At 25° C.

Preparation of 2-thiophenecarboxylideneindene and 2-furanacrylideneindene

Indene reacts with aldehydes to produce benzofulvene derivatives. Currently, reactions of indene with 2-thiophenecarboxaldehyde and 2-furanacrolein were carried out.

The preparation of the sulfur-containing benzofulvene compound 2-thiophenecarboxylideneindene involved the reacting of indene/2-thiophenecarboxaldehyde mixtures (3:2 molar ratio) in the presence of methanol/TMAH solutions. In practice, 2-thiophenecarboxaldehyde (39 gms) was added dropwise to a solution of indene (59 gms), methanol (200 ml) and TMAH (55.8 gms of 20 percent TMAH in methanol). After stirring for one hour, a dark-yellow product (melting point approximately 75°C) was collected. Mass spectrometry data supported the proposed structure for the benzofulvene product (molecular weight of 210).

2-thiophenecarboxylideneindene

2-furanacrylideneindene

The differential thermal analysis (DTA) scan indicates an endotherm associated with fusion in the range 63 to 106°C and a polymerization exotherm of 165 to 250°C .

A second benzofulvene compound (2-furanacrylideneindene) was prepared by the addition of 2-furanacrolein (23 gms) to a solution of indene (58 gms)/methanol (200 ml)/TMAH (55.8 gms). After one hour's stirring, an orange product (melting point of approximately 95°C) was collected by filtration and dried. The proposed structure (molecular weight of 220) was supported by mass spectrometry data. The DTA scan showed a fusion endotherm at 76 to 115°C and a significant polymerization exotherm at 386 to 491°C .

Properties of Carbon Derived from Mixtures of Cinnamylideneindene and Ammonium Acetate

Ammonium acetate (NH_4Ac) was dry blended with cinnamylideneindene (CAI) to see if the CAI-derived carbon properties could be modified in the same manner as was observed for CAI/KAC blends. Carbon data in Table A-12 indicated no significant change in coke yield as the NH_4Ac content increased to 15 percent. As seen in Figure A-32, g-factors decreased to a minimum at approximately ten percent NH_4Ac and then increased.

Table A-12
PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
CINNAMYLIDENEINDENE AND AMMONIUM ACETATE

Sample	NH_4Ac Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d_{004} (Å)	L_c (Å)	gfactor
A	1.0	41	1.6820	130	0.884
B	3.8	32	1.6842	212	0.833
C	5.0	39	1.6894	110	0.712
D	15.0	35	1.6914	100	0.665
E	20.0	33	1.6845	116	0.826

(1) Temperature at $1,000^\circ\text{C}$; samples coked without a prior air cure.

(2) Temperatures at $2,800^\circ\text{C}$.

Figure A-32. g-FACTOR OF CARBONS DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND AMMONIUM ACETATES AS A FUNCTION OF AMMONIUM ACETATE CONTENT.

Microstructures seen in Figure A-33, also show the decrease in crystallinity as the NH_4Ac concentration increases to ten percent. With 15 percent NH_4Ac , Figure A-33(e), a heterogeneous carbon with areas of high and low crystallinity was visible. Thus, the blending of CAI and NH_4Ac allowed some control over the microstructure of the derived carbon.

Properties of Carbon Derived from Blends of Cinnamylideneindene and p-Xylylideneindene

Blends of CAI and p-xylylideneindene (XYN) were carbonized without an air cure to determine if the addition of XYN would allow control over the microstructure of the derived carbon. Carbon data, shown in Table A-13, indicated a decrease in crystallinity of the derived carbon as the XYN content increased. This can be seen in Figure A-34 which shows the variance of the g-factors with XYN content. Carbon yields also gradually increased from 37 to 56 percent.

Microstructures, shown in Figure A-35, also indicated a graduated change from a nonhomogeneous, highly crystalline carbon, Figure A-35(a), to a fine-grained homogeneous carbon, Figure A-35(f). XYN contents greater than 60 percent resulted in nongraphitic carbons.

Thus, the graphitic properties of CAI-derived carbon were significantly influenced by the presence of XYN and could be controlled by the inclusion of XYN.

Properties of Carbon Derived from Mixtures of Cinnamylideneindene and Furfurylideneindene

Blends of furfurylideneindene (FAI) and cinnamylideneindene were carbonized without an air cure to determine if carbon property control could be obtained. A poorly graphitized carbon is obtained from FAI, while CAI (with low potassium content) yields a more graphitic carbon. Coke yield values increased steadily from 32 to 48 percent as the FAI content increased from 0 to 48 percent (Table A-14 and Figure A-36). There was a gradual decrease in the crystallinity of the carbons as the FAI content increased, reflected in the variance of g-factors (Figure A-36) and interlayer spacing (d_{004}) values (Table A-14).

Microstructures of carbons from these mixtures, as shown in Figure A-37, also indicated the influence of FAI on CAI-derived carbons. A highly crystalline carbon was obtained from CAI with zero percent FAI, Figure A-37(a), and crystallinity gradually decreased upon addition of 10 to 20 percent FAI, Figure A-37(b) and (c). A significant change to a homogeneous, less-crystalline carbon occurred upon addition of 30 percent FAI, Figure A-37(d), and carbons containing 40 and 50 percent FAI, Figure A-37(e), and (f),

(a) 1 Percent $\text{NH}_4\text{Ac.}$ H318-9

(b) 3.8 Percent $\text{NH}_4\text{Ac.}$ H118-2

(c) 5 Percent $\text{NH}_4\text{Ac.}$ H191-1

(d) 10 Percent $\text{NH}_4\text{Ac.}$ H191-2

(e) 15 Percent $\text{NH}_4\text{Ac.}$ H191-3

Figure A-33. MICROSTRUCTURES OF CARBONS (AFTER $2,800^\circ\text{C}$) DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND AMMONIUM ACETATE.

Table A-13
 PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
 CINNAMYLIDENEINDENE AND p-XYLYLIDENEINDENE

Sample	<u>p</u> -Xylylideneindene Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₄ (Å)	L _c (Å)	g _{factor}
A	0	37	1.6791	114	0.951
B	10	38	1.6834	147	0.851
C	20	44	1.6854	79	0.805
D	30	44	1.6865	70	0.779
E	40	48	1.6891	63	0.719
F	50	53	1.6917	67	0.658
G	60	56	1.6923	57	0.644

(1) Temperature at 1,000° C; samples coked without a prior air cure.

(2) Temperature at 2,800° C.

Figure A-34. g FACTOR OF CARBONS DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND p-XYLYLIDENEINDENE AS A FUNCTION OF p-XYLYLIDENEINDENE CONTENT.

were even more homogeneous and less crystalline. In summary, the blending of CAI and FAI in varying concentrations allowed control over the microstructure of the derived carbon.

Properties of Carbon Derived from Mixtures of Acenaphthylene and Autoclave-Produced Isotruxene/Truxene

Blends of acenaphthylene (ACN) and autoclave-produced ITX/TX (60% ITX) were carbonized without an air cure to determine if microstructural control of the resulting carbons could be obtained. Previous samples of these blends were coked with an air cure. As seen in Table A-15,

Figure A-35. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND p-XYLYLIDENEINDENE.

Table A-14
 PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
 CINNAMYLIDENEINDENE AND FURFURYLIDENEINDENE

Sample	Furfurylideneindene Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₄ (Å)	L _c (Å)	g _{factor}
A	0	32	1.6814	248	0.898
B	10	36	1.6817	129	0.891
C	20	39	1.6828	142	0.865
D	30	44	1.6862	88	0.786
E	40	46	1.6860	93	0.791
F	50	48	1.6891	103	0.719

(1) Temperature at 1,000° C; samples coked without a prior air cure.

(2) Temperature at 2,800° C.

Figure A-36. COKE YIELD (AFTER 1,000° C) AND g FACTOR (AFTER 2,800° C) OF CARBONS DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND FURFURYLIDENEINDENE AS A FUNCTION OF FURFURYLIDENEINDENE CONTENT.

essentially no change in coke yield occurred. There was, however, an increase in the graphiticity as the ACN concentration increased. Microstructures, shown in Figure A-38, were heterogeneous with large-grain areas (typical of ACN-derived carbons) and areas of finer grain size.

The blending of ACN and autoclave-produced ITX-TX allowed some control over the microstructure of the derived carbon.

Properties of Carbon Derived from Mixtures of Acenaphthylene and Truxene

Blends of acenaphthylene (ACN) and truxene (TX) were carbonized without an air cure to determine if carbon microstructural control could be obtained by controlling the precursor composition. As seen in Table A-16, coke

(a) 0 Percent FAI. H361-1

(b) 10 Percent FAI. H361-2

(c) 20 Percent FAI. H361-3

(d) 30 Percent FAI. H361-4

(e) 40 Percent FAI. H361-5

(f) 50 Percent FAI. H361-6

Figure A-37. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM MIXTURES OF CINNAMYLIDENEINDENE AND FURFURYLIDENEINDENE.

(a) 10 Percent ACN.

H318-3

(b) 20 Percent ACN.

H318-2

(c) 30 Percent ACN.

H318-1

Figure A-38. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM MIXTURES OF ACENAPHTHYLENE AND AUTOCLAVE-PRODUCED ISOTRUXENE/TRUXENE.

Table A-15
 PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
 ACENAPHTHYLENE AND AUTOCLAVE-PRODUCED
 ISOTRUXENE/TRUXENE⁽¹⁾

Sample	Acenaphthylene Content (%)	Coke Yield ⁽²⁾ (%)	Carbon Data ⁽³⁾		
			d ₀₀₄ (Å)	L _c (Å)	g _{factor}
A	10	52	1.6923	71	0.644
B	20	53	1.6906	71	0.684
C	30	49	1.6894	75	0.712

(1) Prepared by autoclaving indene for six hours at 300° C (300 psi).

(2) Temperature at 1,000° C; samples coked without a prior air cure.

(3) Temperature at 2,800° C.

Table A-16
 PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
 ACENAPHTHYLENE AND TRUXENE

Sample	Truxene Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₄ (Å)	L _c (Å)	g _{factor}
A	20	40	1.6803	196	0.923
B	30	43	1.6822	93	0.879

(1) Temperature at 1,000° C; coked without a prior air cure.

(2) Temperature at 2,800° C.

yield values increased slightly as the TX content increased. The decrease in g-factors as the TX content increased was an indication of lower graphiticity.

Microstructure of carbons derived from these blends, shown in Figure A-39, also revealed a trend toward lower graphiticity as the TX content increased. Both carbons were quite heterogeneous, with areas of high crystallinity as well as areas of noncrystallinity apparent in both samples. In summary, microstructures of carbon derived from ACN are affected by the inclusion of TX.

(a) 20 Percent Truxene.

H320-3

(b) 30 Percent Truxene.

H320-4

Figure A-39. MICROSTRUCTURES OF CARBONS (AFTER 2,800°C) DERIVED FROM MIXTURES OF ACENAPHTHYLENE AND TRUXENE.

Properties of Carbon Derived from Mixtures of Autoclave-Produced Isotruxene/Truxene and Pyromellitic Dianhydride

Blends of autoclave-produced ITX/TX (60% ITX) and pyromellitic dianhydride (PMDA) were carbonized without an air cure to determine if PMDA modified the derived carbon structure. Carbon data are presented in Table A-17. From Figure A-40 it can be seen that coke yields gradually increased for PMDA concentrations higher than 15 percent. The graphiticity (Figure A-41) of the derived carbons increased as the PMDA concentration increased to 20 percent, and then rapidly decreased for higher PMDA concentrations. Samples containing more than 30 percent PMDA were nongraphitic. This trend was also indicated in photomicrographs shown in Figure A-42. The sample with five percent PMDA was quite heterogeneous, with both high- and low-crystalline areas present, Figure A-41(a). As the PMDA content increased to 10, Figure A-42(b), and 15 percent, Figure A-42(c), the areas of high crystallinity increased in size and proportion. With 20 percent PMDA, Figure A-42(d), a highly crystalline carbon was obtained, with very few lower crystalline areas. The highly crystalline areas decreased as the PMDA content was increased to 30 percent, Figure A-42(e), and a noncrystalline structure was obtained when the PMDA concentration was increased to 40 percent, Figure A-42(f).

In summary, the addition of PMDA to autoclave-produced ITX/TX did allow some control over the microstructure of the derived carbon, though the carbon structures were quite heterogeneous.

Effect of Autoclave-Hold Time on Carbons Derived from Cinnamylideneindene

Cinnamylideneindene was autoclaved at 300° C and 300 psi for varying times to determine if the microstructure of derived carbon was altered. Carbon data are presented in Table A-18. The molecular weight of the resulting polymers was not significantly altered as the autoclave-hold times increased. Coke-yield values, shown in Table A-18 and Figure A-43, increased irregularly for both the air-cured and uncured samples. As shown in Figure A-44, g-factors for both the cured and uncured samples do not appear to change significantly with longer autoclave-treatment times.

Microstructures of the derived carbons were only slightly altered by the longer hold times. Carbons from CAI polymers coked with an air cure were of very low graphiticity, Figure A-45(a), while carbons from the CAI polymers coked without an air cure were highly crystalline, Figure A-45(b).

Thus, the microstructure of the CAI-derived carbon was not a function of autoclave-heating time.

Table A-17

PROPERTIES OF CARBON DERIVED FROM MIXTURES OF
AUTOCLAVE-PRODUCED ISOTRUXENE/TRUXENE AND
PYROMELLITIC DIANHYDRIDE (PMDA)

Sample	PMDA Content (%)	Coke Yield ⁽¹⁾ (%)	Carbon Data ⁽²⁾		
			d ₀₀₄ (Å)	L _c (Å)	g _{factor}
A	5	53	1.6952	87	0.577
B	10	52	1.6914	86	0.665
C	15	53	1.6879	112	0.747
D	20	59	1.6836	106	0.847
E	30	56	1.6857	100	0.798
F	40	66	Nongraphitic	-	-

(1) Temperature at 1,000° C; coked without a prior air cure.

(2) Temperature at 2,800° C.

Figure A-40. COKE YIELD (AFTER 1,000° C) OF CARBONS DERIVED FROM MIXTURES OF AUTOCLAVE-PRODUCED ISOTRUXENE/TRUXENE AND PYROMELLITIC DIANHYDRIDE (PMDA) AS A FUNCTION OF PMDA CONTENT.

Carbon Derived from Autoclaved Mixtures of Cinnamaldehyde, Indene, and Terephthalaldehyde

Indene (116 gms)/cinnamaldehyde (132 gms) mixtures were blended with 0, 0.05, and 0.10 mole of terephthalaldehyde and autoclaved for four hours at 300° C and 300 psi. The resulting polymers were carbonized with and without an air cure to determine if the inclusion of terephthalaldehyde altered the derived carbon. As seen from carbon data in Table A-19, coke-yield values increased by a factor of two as the terephthalaldehyde increased from

Figure A-41. g FACTOR OF CARBONS DERIVED FROM MIXTURES OF AUTOCLAVE-PRODUCED ISOTRUXENE/TRUXENE AND PYROMELLITIC DIANHYDRIDE (PMDA) AS A FUNCTION OF PMDA CONTENT.

0 to 0.05 mole. Microstructures for the derived carbons indicate decreasing graphiticity as the terephthalaldehyde content increased for the samples coked without an air cure (Figure A-46). After coking with an air cure, a fine-grained microstructure was obtained from the sample containing no terephthalaldehyde, Figure A-47(a), while the samples with 0.05 and 0.1 mole of terephthalaldehyde were noncrystalline, Figures A-47(b) and (c). Therefore, autoclaving mixtures of indene and cinnamaldehyde with varying amounts of terephthalaldehyde appeared to be one method of carbon property control.

Polymerization of Cinnamaldehyde/Indene Mixtures

Data suggested that low-viscosity binders having nominal coke yields could be prepared by autoclave polymerization of cinnamaldehyde/indene mixtures. Using this approach, binders are more easily prepared than from CAI/indene mixtures since the latter requires preparation or procurement of CAI in addition to an autoclave polymerization step and a subsequent blending step. Coke yields of the cinnamaldehyde/indene polymers were comparable or higher than those of CAI/indene binder systems containing 50 phr indene monomer. Further evaluation of cinnamaldehyde/indene mixtures with molar ratios of 0.67, 1.0, 1.5, and 2.0 heated at various autoclave temperatures was continued. After examining the physical properties of the resulting polymers, samples were carbonized both with and without a prior air cure. Data obtained during this study are summarized in Table A-20.

For samples having a cinnamaldehyde/indene ratio of 0.67, minima in the average molecular weight (Figure A-48) and viscosity data were observed with increasing autoclave temperature. These minima occurred at approximately 300° C. Coke yields for these polymers were higher for samples that were air cured prior to carbonization (Figure A-49) and gradually increased with increased autoclave temperatures. Inflections in the curve appeared for

(a) 5 Percent PMDA. H118-3

(b) 10 Percent PMDA. H118-4

(c) 15 Percent PMDA. H118-5

(d) 20 Percent PMDA. H319-2

(e) 30 Percent PMDA. H319-3

(f) 40 Percent PMDA. H319-4

Figure A-42. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM MIXTURES OF AUTOCLAVE-PRODUCED ISOTRUXENE/TRUXENE AND PYROMELLITIC DIANHYDRIDE.

Table A-18
 PROPERTIES OF POLYMERS PREPARED BY AUTOCLAVING CINNAMYLIDENEINDENE⁽¹⁾

Sample	Autoclave Hold Time (hrs)	Coke Yield ⁽²⁾		Average Molecular Weight ⁽³⁾	Carbon Data ⁽⁴⁾					
		With Air Cure	Without Air Cure		d ₀₀₄ (Å)		L _c (Å)		gfactor	
					With Air Cure	Without Air Cure	With Air Cure	Without Air Cure	With Air Cure	Without Air Cure
A	2	58	44	421	1.7007	1.6831	89	230	0.449	0.858
B	4	56	44	424	1.7010	1.6839	110	219	0.442	0.840
C	6	51	39	458	1.6978	1.6842	121	228	0.516	0.833
D	10	57	45	422	1.6969	1.6831	120	214	0.537	0.858
E	16	59	46	424	1.6958	1.6831	97	238	0.563	0.858
F	18	65	49	457	1.7028	1.6825	96	175	0.400	0.872
G	20	65	51	479	1.6989	1.6825	101	160	0.491	0.872
H	22	62	48	464	1.6975	1.6857	96	137	0.523	0.798
I	24	64	49	455	1.7013	1.6865	72	149	0.434	0.779

(1) Heated at 300° C, 300 psi for indicated times.

(2) Temperature at 1,000° C.

(3) Determined by vapor pressure osmometry.

(4) Temperature at 2,800° C.

Figure A-43. COKE YIELD (AFTER 1,000° C) OF POLYMERS PREPARED BY AUTOCLAVING CINNAMYLIDENEINDENE.

Figure A-44. g FACTOR OF CARBONS DERIVED FROM POLYMERS PREPARED BY AUTOCLAVING CINNAMYLIDENEINDENE.

samples autoclaved at 300° C. This also reflects the lower average molecular weight value obtained for these 300° C samples. A minimum g-factor value was observed for air-cured samples, while g-factors for samples coked without an air cure increased gradually with increased autoclave temperature (Figure A-50). This trend can be seen in the microstructures in Figures A-51 and A-52. For samples coked with an air cure, a decrease in crystallinity was evident as the autoclave treatment increased from 200 to 250° C, Figures A-51(a) and (b), after which the carbons became increasingly crystalline as the temperature increased to 300 and 340° C, Figures A-51(c) and (d). For the samples coked without an air cure, a gradual increase in crystallinity was evident as the autoclave temperature increased (Figure A-52).

Further polymerization studies of the cinnamaldehyde/indene system involved altering the cinnamaldehyde/indene mole ratio at autoclave temperatures of 300 and 340° C (Table A-20).

(a) Coked With a Prior Air Cure.

H189-1

(b) Coked Without a Prior Air Cure.

H189-2

Figure A-45. MICROSTRUCTURES TYPICAL OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-POLYMERIZED (300° C, 300 PSI, 18 HOURS) CINNAMYLIDENEINDENE

Table A-19
 PROPERTIES OF POLYMERS PREPARED BY AUTOCLAVING MIXTURES OF
 CINNAMALDEHYDE, INDENE, AND TEREPHTHALALDEHYDE⁽¹⁾

Sample	Terephthalaldehyde Content ⁽²⁾ (moles)	Coke Yield ⁽³⁾ (%)		Carbon Data ⁽⁴⁾					
		With Air Cure	Without Air Cure	d ₀₀₄ (A)		L _c (A)		g _{factor}	
				With Air Cure	Without Air Cure	With Air Cure	Without Air Cure	With Air Cure	Without Air Cure
A	0.00	33	21	1.6943	1.6836	91	219	0.598	0.847
B	0.05	60	42	1.7146	1.6903	48	100	0.127	0.691
C	0.10	58	47	1.7004	1.6923	58	89	0.456	0.644

(1) Samples heated at 300° C, 300 psi for four hours.

(2) Samples contained 116 grams indene, 132 grams cinnamaldehyde, and indicated amount of terephthalaldehyde.

(3) Temperature at 1,000° C.

(4) Temperature at 2,800° C.

(a) 0 Mole Terephthalaldehyde.

H6-10

(b) 0.05 Mole Terephthalaldehyde.

H190-10

(c) 0.10 Mole Terephthalaldehyde.

H190-12

Figure A-46. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-POLYMERIZED MIXTURES OF CINNAMALDEHYDE/INDENE/TEREPHTHALALDEHYDE COKED WITHOUT AN AIR CURE.

(a) 0 Mole Terephthalaldehyde.

H6-9

(b) 0.05 Mole Terephthalaldehyde.

H190-9

(c) 0.10 Mole Terephthalaldehyde.

H190-11

Figure A-47. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVED-POLYMERIZED MIXTURES OF CINNAMALDEHYDE/INDENE/TEREPHTHALALDEHYDE COKED WITH AN AIR CURE.

Table A-20
PROPERTIES OF POLYMERS PREPARED BY AUTOCLAVING MIXTURES OF CINNAMALDEHYDE AND INDENE

Sample	Cinnamaldehyde/ Indene Mole Ratio	Autoclave Temperature ⁽¹⁾ (° C)	Polymer Average Molecular Weight ⁽²⁾	Polymer Viscosity ⁽³⁾ (centipoises)	Coke Yield ⁽⁴⁾ (%)		Carbon Data ⁽⁵⁾					
					With Air Cure	Without Air Cure	d ₀₀₄ (A)		L _c (A)		g _{factor}	
							With Air Cure	Without Air Cure	With Air Cure	Without Air Cure	With Air Cure	Without Air Cure
A	0.67	200	319	-	25	19	1.6914	1.6857	98	130	0.665	0.798
B	0.67	250	286	900	34	23	1.6923	1.6831	102	173	0.644	0.858
C	0.67	300	276	260	33	22	1.6906	1.6834	103	209	0.684	0.851
D	0.67	340	301	1,840	41	31	1.6857	1.6820	125	268	0.798	0.884
E	1.00	300	277	160	33	21	1.6943	1.6836	91	219	0.598	0.847
F	1.50	300	344	-	55	38	1.7110	1.6865	45	101	0.209	0.779
G	2.00	300	283	120	32	21	1.7098	1.6908	49	98	0.237	0.679
H	1.00	340	400	-	58	46	1.7098	1.6865	66	132	0.237	0.779
I	1.50	340	402	-	62	45	1.7042	1.6860	59	105	0.367	0.791

(1) Mixtures were heated at temperature for four hours.

(2) Determined by vapor pressure osmometry.

(3) Measured at 25° C with a Brookfield viscometer. Where no value is indicated, samples were low melting solids.

(4) Temperature at 1,000° C.

(5) Temperature at 2,800° C.

Figure A-48. AVERAGE MOLECULAR WEIGHT OF AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE MIXTURES AS A FUNCTION OF AUTOCLAVE TREATMENT TEMPERATURE.

Figure A-49. COKE YIELD (AFTER 1,000° C) OF CARBONS DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE MIXTURES AS A FUNCTION OF AUTOCLAVE TREATMENT TEMPERATURE.

For samples autoclaved at 300° C, a maximum in the average molecular weight (Figure A-53) was observed with increasing cinnamaldehyde/indene mole ratio. Corresponding samples autoclaved at 340° C had molecular weights that were higher than those of the 300° C polymers. Average molecular weight values for the 340° C polymers were essentially constant for cinnamaldehyde/indene ratios greater than 1.0.

Coke-yield values for both the 300 and 340° C polymers were higher for samples that were air cured prior to carbonization. For the 300° C polymers, coke yields reached a maximum at a cinnamaldehyde/indene ratio of 1.5 (Figure A-54). Coke-yield values for the 340° C polymers approached a maximum value at a cinnamaldehyde/indene ratio of 2.0 (Figure A-55).

Figure A-50. g-FACTORS OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE AS A FUNCTION OF AUTOCLAVE TREATMENT TEMPERATURE

As can be seen in Figures A-56 and A-57, g-factors of carbons derived from both the 300 and 340° C polymers were much higher for samples coked without a prior air cure. For carbons derived from the 300° C polymers coked with an air cure, a minimum in the g-factors was observed at a cinnamaldehyde/indene ratio of approximately 1.7 (Figure A-56). This decrease in crystallinity was evident in photomicrographs in Figure A-58. For carbons derived from 300° C polymers coked without an air cure, a gradual decrease in crystallinity was observed as the cinnamaldehyde/indene ratio increased. This is evidenced by the decrease in g-factor (Figure A-56) and by the examination of microstructures shown in Figure A-59.

Minimum g-factor values were observed in carbons derived from the 340° C polymers coked with and without an air cure (Figure A-57). These minima occurred at cinnamaldehyde/indene ratios of approximately 1.3. Examination of photomicrographs in Figure A-60 revealed a decrease in noncrystallinity for the carbons derived from the air-cured, 340° C polymers. Noncrystalline carbons were obtained for cinnamaldehyde/indene ratios greater than 1.0. Nonhomogeneous crystalline carbons were obtained from the 340° C polymers coked without an air cure (Figure A-61). Microstructures decreased in crystallinity as the cinnamaldehyde/indene ratio increased from 0.67, Figure A-60(a) to 1.0, Figure A-61(b), and increased in crystallinity as the cinnamaldehyde/indene ratio increased to 1.5, Figure A-60(c).

In summary, low-viscosity binders can be prepared by autoclave polymerization of cinnamaldehyde/indene. Physical properties of these binders are dependent upon cinnamaldehyde/indene reactant ratio and autoclave-treatment temperature and control over these properties appears to be a matter of controlling the aforementioned variables.

(a) 200° C.

H6-1

(b) 250° C.

H6-3

(c) 300° C.

H6-5

(d) 340° C.

H6-7

Figure A-51. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE COKED WITH AN AIR CURE.

(a) 200° C.

H6-2

(b) 250° C.

H6-4

(c) 300° C.

H6-6

(d) 340° C.

H6-8

Figure A-52. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE COKED WITHOUT AN AIR CURE.

Figure A-53. AVERAGE MOLECULAR WEIGHT OF POLYMERS PREPARED BY AUTOCLAVING CINNAMALDEHYDE/INDENE MIXTURES AS A FUNCTION OF CINNAMALDEHYDE/INDENE MOLE RATIO.

Figure A-54. COKE YIELDS (AFTER 1,000° C) OF CARBONS DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 300° C.

Polymerization of Cinnamaldehyde/Indene/Tetramethylammonium Hydroxide Mixture

Further efforts to prepare low-viscosity, nominal coke-yield binders involved the autoclave polymerization of cinnamaldehyde/indene mixtures with 0, 1, 3, and 5 percent tetramethylammonium hydroxide (TMAH). The mixtures were autoclaved at 300° C (300 psi) for four hours and the resulting polymers carbonized with and without an air cure. Data from these studies are presented in Table A-21. Average molecular weight data indicated a graduated increase as the TMAH content increased (Figure A-62). Coke-yield values for both the air-cured and uncured samples increased significantly as the TMAH content increased to one percent (Figure A-63). However, TMAH contents higher than one percent did not significantly alter the coke-yield values.

Figure A-55. COKE YIELD (AFTER 1,000° C) OF CARBONS DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 340° C.

Figure A-56. g FACTOR (AFTER 2,800° C) OF CARBONS DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 300° C.

Figure A-57. g FACTOR OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 340° C.

(a) 0.67 Cinnamaldehyde/Indene Mole Ratio. H6-5

(b) 1.0 Cinnamaldehyde/Indene Mole Ratio. H6-9

(c) 1.5 Cinnamaldehyde/Indene Mole Ratio. H190-5

(d) 2.0 Cinnamaldehyde/Indene Mole Ratio. H6-11

Figure A-58. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) OF CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 300° C. (Coked With an Air Cure)

(a) 0.67 Cinnamaldehyde/Indene Mole Ratio. H6-6

(b) 1.0 Cinnamaldehyde/Indene Mole Ratio. H6-10

(c) 1.5 Cinnamaldehyde/Indene Mole Ratio. H190-6

(d) 2.0 Cinnamaldehyde/Indene Mole Ratio. H6-12

Figure A-59. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED AT 300° C. (Coked Without an Air Cure)

(a) 0.67 Cinnamaldehyde/Indene Mole Ratio. H6-7

(b) 1.0 Cinnamaldehyde/Indene Mole Ratio. H192-7

(c) 1.5 Cinnamaldehyde/Indene Mole Ratio. H190-7

Figure A-60. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED FOR FOUR HOURS AT 340° C. (Coked With an Air Cure)

(a) 0.67 Cinnamaldehyde/Indene Mole Ratio. H190-8

(b) 1.0 Cinnamaldehyde/Indene Mole Ratio. H192-8

(c) 1.5 Cinnamaldehyde/Indene Mole Ratio. H6-8

Figure A-61. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM CINNAMALDEHYDE/INDENE MIXTURES AUTOCLAVE-POLYMERIZED FOR FOUR HOURS AT 340° C. (Coked Without an Air Cure)

Table A-21
 PROPERTIES OF POLYMERS PREPARED BY AUTOCLAVING MIXTURES OF CINNAMALDEHYDE,
 INDENE, AND TETRAMETHYLAMMONIUM HYDROXIDE

Sample ⁽¹⁾	TMAH Content (%)	Polymer Average Molecular Weight ⁽²⁾	Coke Yield ⁽³⁾ (%)		Carbon Data ⁽⁴⁾					
			With Air Cure	Without Air Cure	d ₀₀₄ (A)		L _c (A)		g _{factor}	
					With Air Cure	Without Air Cure	With Air Cure	Without Air Cure	With Air Cure	Without Air Cure
A	0	276	33	21	1.6906	1.6834	103	209	0.684	0.851
B	1	314	55	36	1.7080	1.6848	73	120	0.279	0.819
C	3	352	56	36	1.6989	1.6848	191	91	0.491	0.819
D	5	372	58	41	1.6952	1.6842	86	202	0.577	0.833

(1) Cinnamaldehyde/indene mole ratio constant at 0.67; samples heated at 300° C, 300 psi for four hours.

(2) Determined by vapor pressure osmometry.

(3) Temperature at 1,000° C.

(4) Temperature at 2,800° C.

Figure A-62. AVERAGE MOLECULAR WEIGHT OF AUTO-CLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE/TETRAMETHYLAMMONIUM HYDROXIDE AS A FUNCTION OF TMAH CONTENT.

Figure A-63. COKE YIELD (AFTER 1,000° C) OF AUTO-CLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE/TETRAMETHYLAMMONIUM HYDROXIDE AS A FUNCTION OF TMAH CONTENT.

Figure A-64 indicates the variance of g-factors with TMAH content. For the samples coked with an air cure, a minimum g-factor value was obtained at a TMAH concentration of approximately one percent. This decrease in crystallinity was quite evident in the microstructures shown in Figure A-65. A fine-grained crystalline carbon was obtained from the polymer with zero percent TMAH, Figure A-65(a), while a noncrystalline structure was obtained when the TMAH content increased to one percent, Figure A-65(b). TMAH concentrations of three and five percent, Figure A-65(c), and A-65(d), respectively, resulted in heterogeneous carbons with areas of fine-grained crystallinity and areas of noncrystallinity readily apparent. For the samples coked without an air cure, very little difference was noted in g-factors (Figure A-64) and microstructures (Figure A-66) as the TMAH content increased. A heterogeneous, highly crystalline carbon was obtained from each of these polymers.

Figure A-64. g FACTORS OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE/TETRAMETHYLAMMONIUM HYDROXIDE AS A FUNCTION OF TMAH CONTENT.

Thus, polymers obtained by the autoclave polymerization of cinnamaldehyde/indene/TMAH mixtures had significantly higher coke yields than cinnamaldehyde/indene-based polymers. This is potentially useful in the preparation of binder systems.

Sulfonation of Hydrocarbon Derivatives of Indene Using Chlorosulfonic Acid (ClSO₃H)

The inclusion of sulfonic acid exchange sites in certain hydrocarbon derivatives of indene affords ion exchange materials having high weight yields on pyrolysis. Cinnamylideneindene (CAI), *p*-xylylideneindene (XYN), isotruxene (ITX), and truxene (TX) were sulfonated by dispersing the materials as a slurry in dichloroethane (DiClEt) and adding ClSO₃H/DiClEt solutions dropwise at room temperature. Drop rates were adjusted so that very little warming resulted from the exothermic reactions. After completion of the ClSO₃H/DiClEt addition, residual solids were collected, washed with DiClEt, and dried at 60° C. Data on these reactions are shown in Table A-22.

The reaction sequence may be represented as follows (where Ar denotes an aromatic nucleus):

Excess ClSO₃H (greater than equimolar) may lead to disulfonation or to the production of sulfonyl chloride compounds, depending on temperature, and availability and reactivity of aromatic nuclei. These reactions are depicted below:

(a) Zero Percent TMAH.

H6-5

(b) One Percent TMAH.

H192-1

(c) Three Percent TMAH.

H192-3

(d) Five Percent TMAH.

H192-5

Figure A-65. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE/TETRAMETHYLAMMONIUM HYDROXIDE. (Coked With an Air Cure)

(a) Zero Percent TMAH.

H6-6

(b) One Percent TMAH.

H192-2

(c) Three Percent TMAH.

H192-4

(d) Five Percent TMAH.

H192-6

Figure A-66. MICROSTRUCTURES OF CARBONS (AFTER 2,800° C) DERIVED FROM AUTOCLAVE-PRODUCED POLYMERS OF CINNAMALDEHYDE/INDENE/TETRAMETHYLAMMONIUM HYDROXIDE. (Coked Without an Air Cure)

Table A-22
SULFONATION OF HYDROCARBON DERIVATIVES OF INDENE⁽¹⁾

Batch	Hydrocarbon Material	Reactant Molar Ratio ⁽²⁾	Analysis of As-Prepared Material ⁽³⁾			Analysis ⁽⁴⁾ S (%)	Coke Yield ⁽⁵⁾ (%)
			Cl (%)	O (%)	S (%)		
N-12-14	Cinnamylideneindene	2	0.6	32.1	9.3	4.0	57.3 ⁽⁶⁾
N-12-15	<i>p</i> -Xylylideneindene	2	1.5	28.9	9.8	3.1	64.6 ⁽⁷⁾
N-12-16	Isotrxene	3	0.2	27.4	12.4	6.7	61.6 ⁽⁸⁾
N-12-18	Truxene	3	0.2	29.3	10.4	6.0	56.5 ⁽⁹⁾

(1) Hydrocarbon derivatives were dispersed as a slurry in dichloroethane; chlorosulfonic acid (ClSO₃H) was added dropwise at room temperature.

(2) Ratio (mole ClSO₃H/moles hydrocarbon).

(3) Samples were dried at 60° C prior to analysis; data suggests considerable moisture remained after drying.

(4) After air cure to 300° C; samples were heated in a programmed cycle requiring approximately 120 hours to reach 300° C.

(5) Coke yields (600° C) are those obtained on thermal gravimetric analysis of as-prepared samples (weight loss excludes residual moisture which was removed by evacuation prior to heating).

(6) Sample lost 13.6 percent on evacuation prior to heating.

(7) Sample lost 13.2 percent on evacuation prior to heating.

(8) Sample lost 8.6 percent on evacuation prior to heating.

(9) Sample lost 12.7 percent on evacuation prior to heating.

Studies indicated that considerable moisture was retained by the sulfonated compounds after drying at 60° C. This is suggested by the high oxygen content relative to sulfur (theoretical 3/2 weight ratio for sulfonic acid group) for the 60° C dried materials as shown in Table A-22. Samples subsequently dried at 100° C underwent additional weight loss as did samples that were vacuum outgassed at room temperature (see coke-yield data in Table A-22). Low chlorine content indicated the presence of relatively little sulfonyl chloride contaminant. Contrary to the nature of the hydrocarbon starting materials, the sulfonated materials are infusible but quite soluble in water, as would be expected due to the presence of highly polar, hydrophilic groups, ion-exchange reactions with these materials would, of necessity, require nonaqueous systems. However, heating these sulfonated materials in air renders them insoluble in water. This process apparently promotes cross-linking and results in a reduction in sulfur content (Table A-22) and the hydrophilicity of the materials.

Thermal analysis of the sulfonated hydrocarbons (without an air cure) showed minimal or no differential thermal response as heating apparently results in a slow cross-linking process prohibiting fusion and any intense polymerization exotherms. Coke yields (after 600° C) of the materials were in the range 55 to 65 percent. An air cure prior to carbonization should enhance these values.

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Additional sulfonation reactions were carried out on ITX and CAI by initially dissolving these materials in chloroform, and adding ClSO_3H dropwise to the solution. Data on these reaction products are shown in Table A-23.

Table A-23
SULFONATION OF HYDROCARBON DERIVATIVES OF INDENE⁽¹⁾

Batch	Hydrocarbon Material	Reactant Molar Ratio ⁽²⁾	Sulfur Content (%)
N-11-96A	Isotraxene	1	6.8
N-11-96B	Isotraxene	2	10.5
N-11-97A	Cinnamylideneindene	1	5.7
N-11-97B	Cinnamylideneindene	2	8.0

(1) Hydrocarbon materials were dissolved in chloroform and chlorosulfonic acid (ClSO_3H) was added dropwise at room temperature.

(2) Ratio (moles ClSO_3H /moles hydrocarbon).

Sulfonation decreased the solubility of the hydrocarbons to the point where products could be conveniently collected by filtration. Considerable polymerization of CAI also occurred during sulfonation in solution, and the resulting product had a reduced solubility in water relative to the products sulfonated as a slurry.

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FUTURE OBJECTIVES

The development of an improved NERVA graphite fuel element will be continued. These studies will include fabrication studies using pressure coking operations in an endeavor to improve the matrix quality. Characterization of vapor-deposited zirconium carbide tubes, improved fuel bead and other related subjects will continue to be explored.

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